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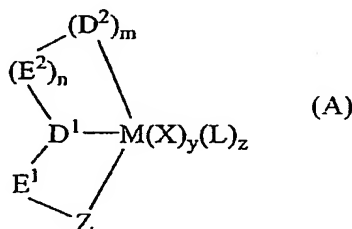
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(54) Title: POLYMERISATION AND OLIGOMERISATION CATALYSTS



(57) Abstract: A polymerisation catalyst comprising (1) a transition metal compound of Formula A, and optionally (2) an activating quantity of a Lewis acid activator, Formula (A), wherein Z is a five-membered heterocyclic group containing at least one carbon atom, at least one nitrogen atom and at least one other hetero atom selected from nitrogen, sulphur and oxygen, the remaining atoms in the ring being nitrogen or carbon; M is a metal from Group 3 to 11 of the Periodic Table or a lanthanide metal; E¹ and E² are divalent groups from (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups and (vi) heterosubstituted derivatives of groups (i) to (v); D¹ and D² are donor groups; X is an anionic group, L is a neutral donor group; n = m = zero or 1; y and z are zero or integers. The catalysts are useful for polymerising or oligomerising 1-olefins.

WO 2004/083263 A1



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POLYMERISATION AND OLIGOMERISATION CATALYSTS

The present invention relates to transition metal-based polymerisation and oligomerisation catalysts and to their use in the polymerisation, copolymerisation and oligomerisation of olefins.

The use of certain transition metal compounds to polymerise 1-olefins, for example, ethylene or propylene, is well established in the prior art. The use of Ziegler-Natta catalysts, for example, those catalysts produced by activating titanium halides with organometallic compounds such as triethylaluminium, is fundamental to many commercial processes for manufacturing polyolefins. Over the last three decades, advances in the technology have led to the development of Ziegler-Natta catalysts which have such high activities that olefin polymers and copolymers containing very low concentrations of residual catalyst can be produced directly in commercial polymerisation processes. The quantities of residual catalyst remaining in the produced polymer are so small as to render unnecessary their separation and removal for most commercial applications. Such processes can be operated by polymerising the monomers in the gas phase, or in solution or in suspension in a liquid hydrocarbon diluent, or, in the case of propylene in bulk.

Commodity polyethylenes are commercially produced in a variety of different types and grades. Homopolymerisation of ethylene with transition metal based catalysts leads to the production of so-called "high density" grades of polyethylene. These polymers have relatively high stiffness and are useful for making articles where inherent rigidity is required. Copolymerisation of ethylene with higher 1-olefins (eg butene, hexene or octene) is employed commercially to provide a wide variety of copolymers

differing in density and in other important physical properties. Particularly important copolymers made by copolymerising ethylene with higher 1-olefins using transition metal based catalysts are the copolymers having a density in the range of 0.91 to 0.93. These copolymers which are generally referred to in the art as "linear low density polyethylene" are in many respects similar to the so-called "low density" polyethylene produced by the high pressure free radical catalysed polymerisation of ethylene. Such polymers and copolymers are used extensively in the manufacture of flexible blown film.

Polypropylenes are also commercially produced in a variety of different types and grades. Homopolymerisation of propylene with transition metal based catalysts leads to the production of grades with a wide variety of applications. Copolymers of propylene with ethylene or terpolymers with ethylene and higher 1-olefins are also useful materials, often used in film applications.

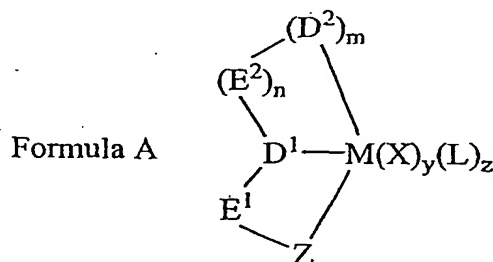
In recent years the use of certain metallocene catalysts (for example biscyclopentadienylzirconiumdichloride-activated with alumoxane) has provided catalysts with potentially high activity. Other derivatives of metallocenes have been shown to be potentially useful for producing polypropylene with good activity, molecular weight and tacticity control. However, metallocene catalysts of this type suffer from a number of disadvantages, for example, high sensitivity to impurities when used with commercially available monomers, diluents and process gas streams, the need to use large quantities of expensive alumoxanes to achieve high activity, difficulties in putting the catalyst on to a suitable support and synthetic difficulties in the production of more complex catalyst structures suitable for polymerising propene in a tactic manner.

Olefin oligomerisation is also a commercially important process, leading to the production of 1-olefins (1-hexene, 1-octene, 1-decene, etc) that find utility in a wide range of applications, for example as comonomers for linear low density polyethylene, monomers for poly(1-olefins) and starting materials for surfactants. Catalysts based on a wide range of metal complexes may be used for this process and typically produce a so-called "Schulz-Flory" distribution of 1-olefins. More recently catalysts have emerged that selectively produce only 1-hexene by a distinctive trimerisation mechanism. Typically the final distribution of 1-olefins produced is of importance commercially.

An object of the present invention is to provide a catalyst suitable for polymerising or oligomerising monomers, for example, olefins, cycloolefins or diolefins, and especially for polymerising or oligomerising ethylene alone or propylene alone, or for copolymerising ethylene with higher 1-olefins with high activity. A further object of the invention is to provide an improved process for the polymerisation of olefins. Yet another object of the present invention is to provide novel complexes based on certain transition metals. The catalysts described here show extremely high activity for polymerisation and oligomerisation which leads to many benefits including lower catalyst loadings in a commercial process and lower catalyst residues in the final product.

The present invention provides a novel polymerisation catalyst comprising

- (1) a transition metal compound having the following Formula A, and optionally
- (2) an activating quantity of a suitable activator,

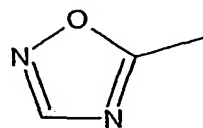
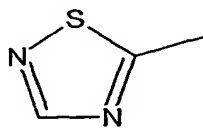
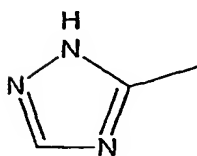
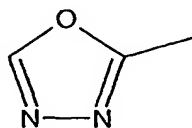
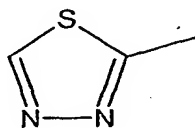
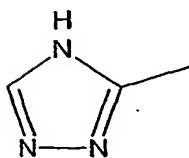
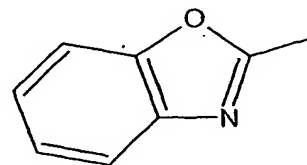
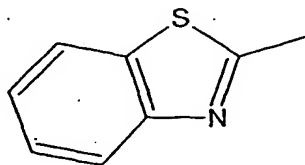
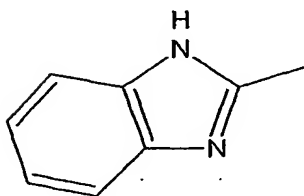
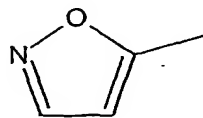
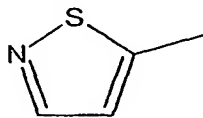
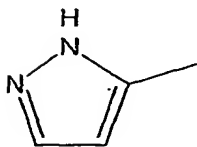
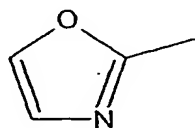
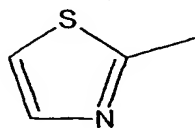
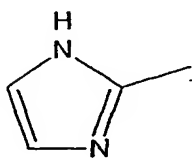


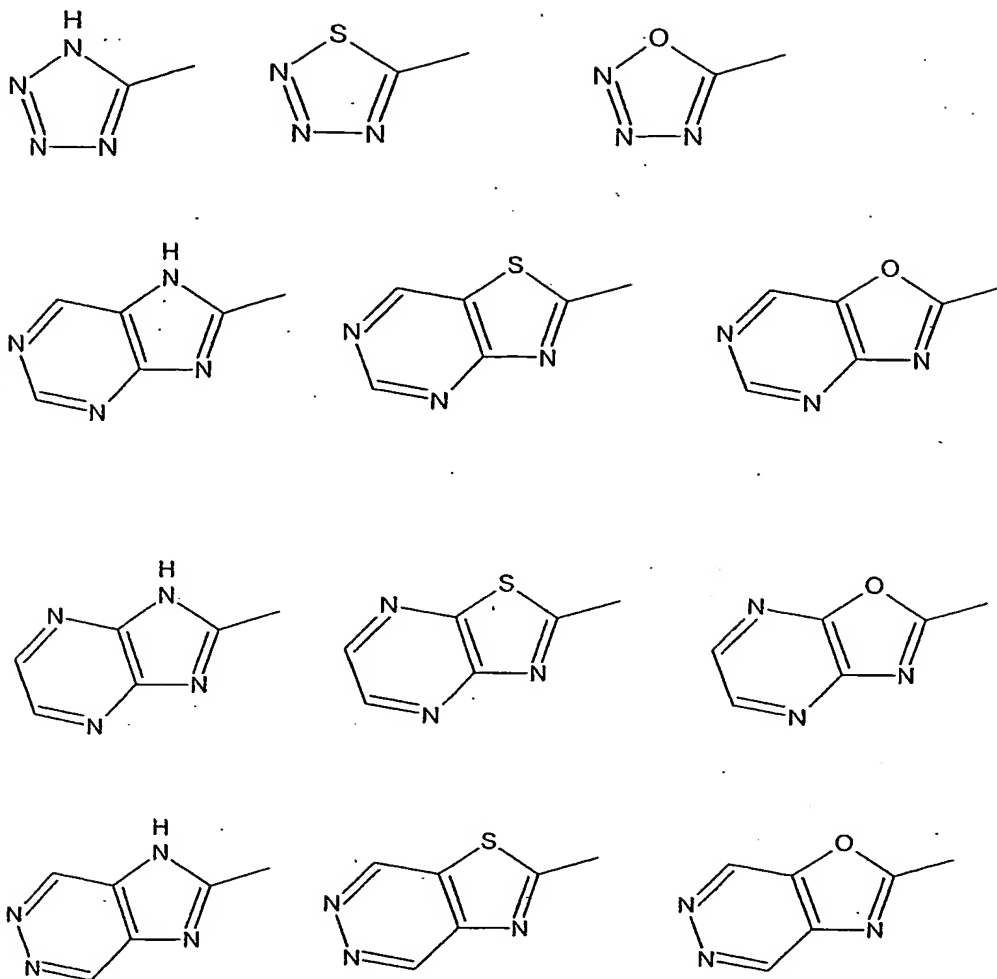
wherein Z comprises a five-membered heterocyclic group, the five membered heterocyclic group containing at least one carbon atom, at least one nitrogen atom and at least one other hetero atom selected from nitrogen, sulphur and oxygen, the remaining atoms in said ring being selected from nitrogen and carbon; M is a metal from Group 3 to 11 of the Periodic Table or a lanthanide metal; E¹ and E² are divalent groups independently selected from (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups and (vi) heterosubstituted derivatives of said groups (i) to (v); D¹ and D² are donor atoms or groups; X is an anionic group, L is a neutral donor group; n = m = zero or 1; y and z are independently zero or integers such that the number of X and L groups satisfy the valency and oxidation state of the metal M.

Preferably the divalent groups E^1 and E^2 are not linked other than through the donor atom or group D^1 .

At least one of the atoms present in the ring of the five-membered heterocyclic group Z is preferably bonded directly to E^1 and preferably a second atom in the ring is bonded directly to M. Most preferably the atom in the five-membered ring bonded directly to E^1 is adjacent to a second atom in said ring, said second atom being bonded directly to M.

The five-membered heterocyclic group Z preferably contains at least 2 carbon atoms in its ring and more preferably at least 3 carbon atoms in its ring. Examples of suitable 5-membered heterocyclic groups are (but are not restricted to):





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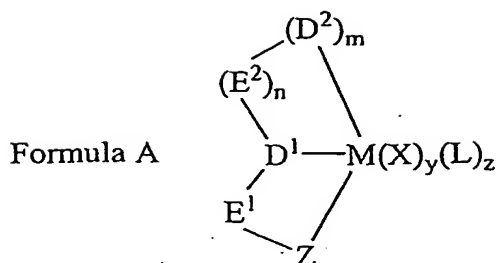
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In a preferred embodiment of the present invention Z, in Formula A, is specifically an imidazole-containing group

Thus, the present invention further provides a novel polymerisation catalyst comprising

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- (1) a transition metal compound having the following Formula A, and optionally
- (2) an activating quantity of a suitable activator,

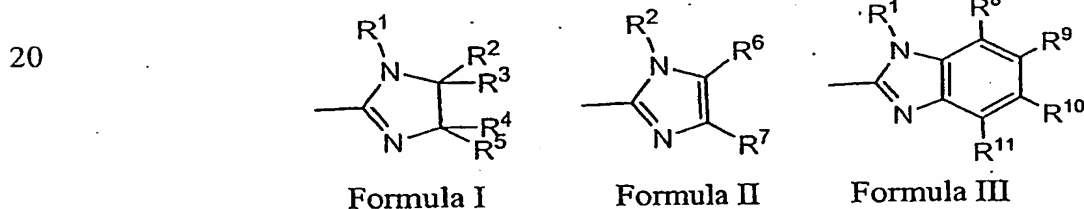


wherein Z is specifically an imidazole-containing group; M is a metal from Group 3 to 11 of the Periodic Table or a lanthanide metal; E¹ and E² are divalent groups

- 5 independently selected from (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups and (vi) heterosubstituted derivatives of said groups (i) to (v); D¹ and D² are donor groups; X is an anionic group, L is a neutral donor group; n = m = zero or 1; y and z are independently zero or integers such that the number of X and L groups satisfy the valency and oxidation state of the metal M.

D¹ and / or D² are donor atoms or groups containing at least one donor atom. D¹ and / or D² can be, for example, groups having the same formula as recited for group Z. For example D¹ and / or D² can be groups comprising a five-membered heterocyclic group containing at least 2 carbon atoms in its ring and more preferably at least 3 carbon atoms in its ring. D¹ and / or D² can be imidazole-containing groups if desired. When D¹ and / or D² are an imidazole-containing group this or these can be identical with Z. In a preferred embodiment D² and Z are identical imidazole containing groups.

The imidazole-containing group Z is preferably a group of formula I, II or III.



- R¹ to R¹¹ are independently hydrogen or a monovalent (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), and (vii) hydrocarbyl-substituted heteroatom groups. The "free" valence bond on the left of Formulae I, II and III provides at least one of the links of E into the rest of

Formula A. The other link or links are preferably provided by at least one of the nitrogen atoms in the imidazole-containing group. These defined groups R^1 to R^{11} preferably contain 1 to 30, more preferably 2 to 20, most preferably 2 to 12 carbon atoms. Examples of suitable aliphatic hydrocarbon groups are methyl, ethyl, ethylenyl, butyl, hexyl, isopropyl and tert-butyl. Examples of suitable alicyclic hydrocarbon groups are adamantyl, norbornyl, cyclopentyl and cyclohexyl. Examples of suitable aromatic hydrocarbon groups are phenyl, biphenyl, naphthyl, phenanthryl and anthryl. Examples of suitable alkyl substituted aromatic hydrocarbon groups are benzyl, tolyl, mesityl, 2,6-diisopropylphenyl and 2,4,6-triisopropyl. Examples of suitable heterocyclic groups are 2-pyridinyl, 3-pyridinyl, 2-thiophenyl, 2-furanyl, 2-pyrrolyl, 2-quinolinyl. Suitable substituents for forming heterosubstituted derivatives of said groups R^1 to R^{11} are, for example, chloro, bromo, fluoro, iodo, nitro, amino, cyano, ether, hydroxyl and silyl, methoxy, ethoxy, phenoxy (i.e. $-\text{OC}_6\text{H}_5$), tolyloxy (i.e. $-\text{OC}_6\text{H}_4(\text{CH}_3)$), xylyloxy, mesityloxy, dimethylamino, diethylamino, methylethylamino, thiomethyl, thiophenyl and trimethylsilyl. Examples of suitable heterosubstituted derivatives of said groups (i) to (v) are 2-chloroethyl, 2-bromocyclohexyl, 2-nitrophenyl, 4-ethoxyphenyl, 4-chloro-2-pyridinyl, 4-dimethylaminophenyl and 4-methylaminophenyl. Examples of suitable hydrocarbyl-substituted heteroatom groups are chloro, bromo, fluoro, iodo, nitro, amino, cyano, ether, hydroxyl and silyl, methoxy, ethoxy, phenoxy (i.e. $-\text{OC}_6\text{H}_5$), tolyloxy (i.e. $-\text{OC}_6\text{H}_4(\text{CH}_3)$), xylyloxy, mesityloxy, dimethylamino, diethylamino, methylethylamino, thiomethyl, thiophenyl and trimethylsilyl. Any of the substituents R^1 to R^{11} may be linked to form cyclic structures. Substituents R^2 to R^{11} may also suitably be inorganic groups such as fluoro, chloro, bromo, iodo, nitro, amino, cyano and hydroxyl.

Further suitable imidazole-containing groups may be obtained by removal of substituent R_1 , for example by deprotonation when R^1 is hydrogen, to give formally monoanionic imidazole-containing groups.

It is preferred that the imidazole-containing group has a structure described in formula III (a "benzimidazole"). R^1 is preferably hydrogen, an aliphatic hydrocarbon group, an aromatic hydrocarbon group or is removed to give a formally monoanionic benzimidazole group. R^8 to R^{11} are preferably hydrogen, an aliphatic hydrocarbon group or an aromatic hydrocarbon group.

E^1 and E^2 (hereinafter referred to as "E") can be the same or different. E is

independently selected from divalent (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), and (vii) hydrocarbyl-substituted heteroatom groups. Examples of suitable divalent groups E are
 5 -CH₂-, -CH₂CH₂-, -CH₂CH₂CH₂-, 1,2-phenylene, *trans*-1,2-cyclopentane, *trans*-1,2-cyclohexane, 2,3-butane, 1,1'-biphenyl, 1,1'-binaphthyl, and -Si(Me)₂-. It is preferred that E is an aliphatic or aromatic hydrocarbon group. More preferably the divalent group E is -CH₂-.

D¹ and D² can be the same or different donor groups, for example oxygen, sulfur, an amine, an imine or a phosphine. Preferably D¹ and D² are selected from
 10 oxygen, sulfur, an amine of formula -N(R¹²)- or a phosphine of formula -P(R¹³)- wherein R¹² and R¹³ are hydrogen or (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), (vii)
 15 hydrocarbyl-substituted heteroatom groups and (viii) further imidazole-containing groups. Alternatively R¹² or R¹³ may be removed, for example by deprotonation when they are hydrogen, to give a formally monoanionic fragment; or if both R¹² or R¹³ are removed they provide a formally dianionic fragment. More preferably D² is an amine of formula -N(R¹²)- as defined above. R¹² is preferably hydrogen, an aliphatic
 20 hydrocarbon, an aromatic hydrocarbon or a further imidazole containing group. Preferably D² is an imidazole-containing group.

M is preferably a metal selected from Groups 3 to 11 of the periodic table, preferably from Groups 3 to 7, more preferably selected from Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn and most preferably V, Cr, Ti, Zr and Hf

25 The anionic group X can be, for example, a halide, preferably chloride or bromide; or a hydrocarbyl group, for example, methyl, benzyl or phenyl; a carboxylate, for example, acetate or an acetylacetonate; an oxide; an amide, for example diethyl amide; an alkoxide, for example, methoxide, ethoxide or phenoxide; or a hydroxyl. Alternatively, X can be a non-coordinating or weakly-coordinating anion, for example,
 30 tetrafluoroborate, a fluorinated aryl borate or a triflate. The anionic groups X may be the same or different and may independently be monoanionic, dianionic or trianionic.

The neutral donor group L can be, for example, a solvate molecule, for example

diethyl ether or THF; an amine, for example, diethyl amine, trimethylamine or pyridine; a phosphine, for example trimethyl phosphine or triphenyl phosphine; or water; or an olefin or a neutral, conjugated or nonconjugated diene, optionally substituted with one or more groups selected from hydrocarbyl or trimethylsilyl groups, said group having up to 40 carbon atoms and forming a pi-complex with M. When L is a diene ligand, it can be, for example s-trans- η^4 -1,4-diphenyl-1,3-butadiene; s-trans- η^4 -3-methyl-1,3-pentadiene; s-trans- η^4 -1,4-dibenzyl-1,3-butadiene; s-trans- η^4 -2,4-hexadiene; s-trans- η^4 -1,3-pentadiene; s-trans- η^4 -1,4-ditolyl-1,3-butadiene; s-trans- η^4 -1,4-bis(trimethylsilyl)-1,3-butadiene; s-trans- η^4 -1,4-diphenyl-1,3-butadiene; s-cis- η^4 -3-methyl-1,3-pentadiene; s-cis- η^4 -1,4-dibenzyl-1,3-butadiene; s-cis- η^4 -2,4-hexadiene; s-cis- η^4 -1,3-pentadiene; s-cis- η^4 -1,4-ditolyl-1,3-butadiene; or s-cis- η^4 -1,4-bis(trimethylsilyl)-1,3-butadiene, said s-cis isomers forming a pi-bound diene complex;

The value of y depends on the formal charge on each group Z and D, the charge on the anionic group X and the oxidation state of the metal M. For example, if M is chromium in oxidation state +3, Z is a neutral group and both D groups are neutral, then y is 3 if X is a monoanionic group (eg. chloride); if M is chromium in oxidation state +3, the Z group is neutral, one D group is monoanionic and the other D is neutral, then y is 2 if all X groups are monoanionic groups (e.g. chloride).

The optional activator (2) for the catalyst of the present invention is suitably selected from organoaluminium compounds and organoboron compounds or mixtures thereof. Examples of organoaluminium compounds include trialkylaluminium compounds, for example, trimethylaluminium, triethylaluminium, tributylaluminium, tri-n-octylaluminium, ethylaluminium dichloride, diethylaluminium chloride, tris(pentafluorophenyl)aluminium and alumoxanes. Alumoxanes are well known in the art as typically the oligomeric compounds which can be prepared by the controlled addition of water to an alkylaluminium compound, for example trimethylaluminium. Such compounds can be linear, cyclic or mixtures thereof. Commercially available alumoxanes are generally believed to be mixtures of linear, cyclic and cage compounds. The cyclic alumoxanes can be represented by the formula $[R^{16}AlO]_s$ and the linear alumoxanes by the formula $R^{17}(R^{18}AlO)_s$ wherein s is a number from about 2 to 50, and wherein R^{16} , R^{17} , and R^{18} represent hydrocarbyl groups, preferably C_1 to C_6 alkyl groups, for example methyl, ethyl or butyl groups.

Examples of suitable organoboron compounds are dimethylphenylammoniumtetra(phenyl)borate, trityltetra(phenyl)borate, triphenylboron, dimethylphenylammonium tetra(pentafluorophenyl)borate, sodium tetrakis[(bis-3,5-trifluoromethyl)phenyl]borate, $H^+(OEt_2)[(bis-3,5-$
5 trifluoromethyl)phenyl]borate, trityltetra(pentafluorophenyl)borate and tris(pentafluorophenyl) boron. Mixtures of organoaluminium compounds and organoboron compounds may be used.

In the preparation of the catalysts of the present invention the quantity of activating compound selected from organoaluminium compounds and organoboron
10 compounds to be employed is easily determined by simple testing, for example, by the preparation of small test samples which can be used to polymerise small quantities of the monomer(s) and thus to determine the activity of the produced catalyst. It is generally found that the quantity employed is sufficient to provide 0.1 to 20,000 atoms, preferably 1 to 2000 atoms of aluminium or boron per atom of M present in
15 the compound of Formula A. Mixtures of different activating compounds may be used.

EP1238989 discloses the use of activators (Lewis acids) selected from
(b-1) ionic-bonding compounds having a $CdCl_2$ type or a CdI_2 type of layered
crystal structure;
(b-2) clays, clay minerals, or ion-exchange layered compounds;
20 (b-3) heteropoly-compounds; and
(b-4) halogenated lanthanoid compounds.

The activator employed in the present invention may be of the type disclosed in EP1238989 if desired. Such Lewis acids are those compounds which capable of receiving at least one electron pair and is capable of forming an ion pair by reaction with
25 the transition metal complex. The Lewis acid includes the afore-mentioned (b-1) ionic-bonding compounds having a layered crystal structure of a $CdCl_2$ type or CdI_2 type (b-2) clay, clay minerals, or ion-exchange layered compounds, (b-3) heteropoly compounds, and (b-4) halogenated lanthanoid compounds. The Lewis acid further includes SiO_2 , Al_2O_3 , natural and synthetic zeolites which have Lewis acid points formed by heating or
30 a like treatment, and complexes and mixtures thereof.

US Patent 6399535 discloses a coordinating catalyst system capable of polymerizing olefins comprising:

(I) as a pre-catalyst, at least one non-metallocene, non-constrained geometry, bidentate ligand containing transition metal compound or tridentate ligand containing transition metal compound capable of (A) being activated upon contact with the catalyst support-activator agglomerate of (II) or (B) being converted, upon contact with an

organometallic compound, to an intermediate capable of being activated upon contact with the catalyst support-activator agglomerate of (II), wherein the transition metal is at least one member selected from Groups 3 to 10 of the Periodic table; in intimate contact with

(II) catalyst support-activator agglomerate comprising a composite of (A) at least one inorganic oxide component selected from SiO_2 , Al_2O_3 , MgO , AlPO_4 , TiO_2 , ZrO_2 , and Cr_2O_3 and (B) at least one ion containing layered material having interspaces between the layers and sufficient Lewis acidity, when present within the catalyst support-

activator agglomerate, to activate the pre-catalyst when the pre-catalyst is in contact with the catalyst support-activator agglomerate, said layered material having a cationic

component and an anionic component, wherein said cationic component is present within the interspaces of the layered material, said layered material being intimately

associated with said inorganic oxide component within the agglomerate in an amount sufficient to improve the activity of the coordinating catalyst system for polymerizing

ethylene monomer, expressed as Kg of polyethylene per gram of catalyst system per

hour, relative to the activity of a corresponding catalyst system employing the same pre-catalyst but in the absence of either Component A or B of the catalyst support-activator agglomerate; wherein the amounts of the pre-catalyst and catalyst support-activator

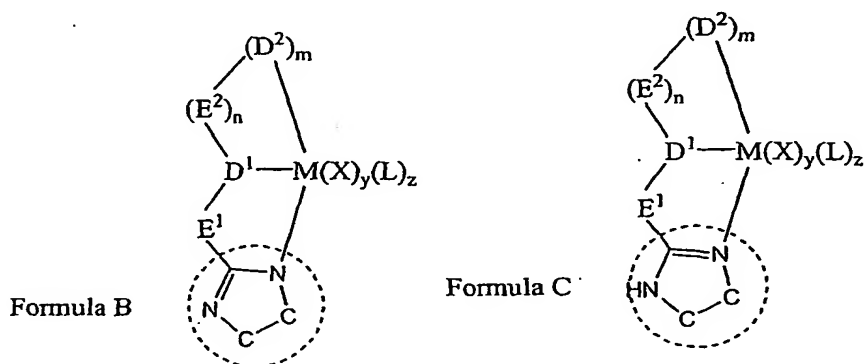
agglomerate which are in intimate contact are sufficient to provide a ratio of micromoles of pre-catalyst to grams of catalyst support-activator agglomerate of from about 5:1 to

about 500:1. The layered material can be, for example, a smectite clay. The catalyst system of the present invention can be employed with a catalyst support-activator agglomerate as described in US 6399535 if desired.

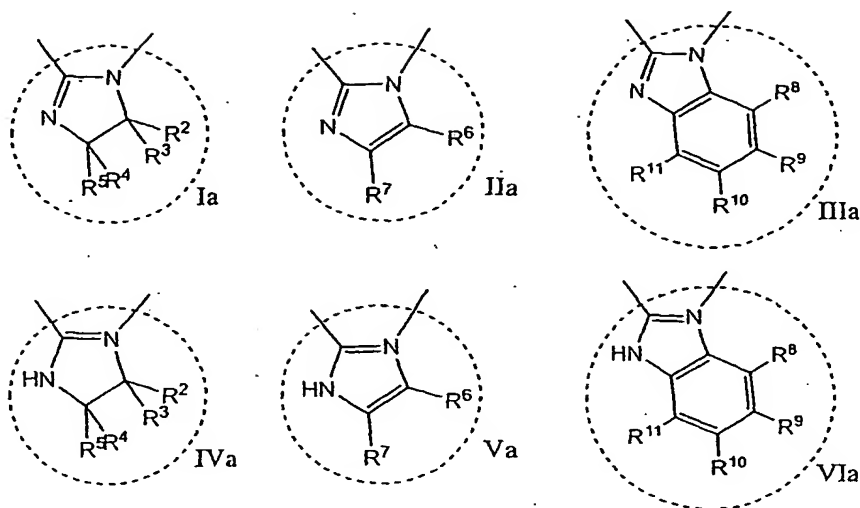
In addition to the activator compound, it can be advantageous to employ catalytic quantities of certain halogenated compounds that are capable of promoting catalyst activity. Promoters of this type are especially useful in the case that the transition metal in the complex is vanadium. US Patent 5191042 discloses that certain vanadium-based catalysts activated with organoaluminium compounds can be promoted

using a variety of halogenated organic compounds, for example, carbon tetrachloride, hexachloroethylene, benzylbromide, benzylchloride and 2,3- or 1,3-dichloropropylene. Other examples of halogenated organic compounds that can be used in this manner are ethyl trichloroacetate, chloroform (CHCl_3) and *n*-butylchloride. US Patent.5191042 also refers to the disclosure of Cooper (T. A Cooper, Journ. Am. Chem. Soc., 4158 (1973), which defines in Table 1 an organic halide activity index based on the ability of the halide to oxidize certain vanadium compounds under standard conditions. For example, carbon tetrachloride is assigned a reactivity of 1 in tetrahydrofuran at 20 °C., and other listed halogenated organic compounds have reactivities of from about 0.02 to greater than 200 relative to carbon tetrachloride. When it is desired to use a halogenated promotor, it is preferred to use those having a Cooper Index ranging from about 0.01 up to about 30. The use of such promoters, especially in combination with vanadium-based catalysts is generally well known in the art, and for details of use of the such promoters reference may be made to US Patent.5191042 and to other prior art in this field. In the present invention it is possible to employ any halogenated organic compound as a promoter, but the compounds mentioned above are preferred.

A preferred embodiment of the present invention provides a catalyst comprising (1) a transition metal compound having the following Formula B or C, and optionally (2) an activating quantity of a suitable activator,



wherein the imidazole nucleus shown within the dotted circle is selected from the divalent groups represented by the Formulae Ia, IIa, IIIa, IVa, Va and VIa,



wherein M is a metal from Group 3 to 11 of the Periodic Table or a lanthanide metal; E¹ and E² are divalent groups independently selected from (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups and (vi) heterosubstituted derivatives of said groups (i) to (v); D¹ and D² are donor groups; X is an anionic group, L is a neutral donor group; n = m = zero or 1; y and z are independently zero or integers such that the number of X and L groups satisfy the valency and oxidation state of the metal M, wherein the groups R² to R¹¹ are independently hydrogen or a monovalent (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), and (vii) hydrocarbyl-substituted heteroatom groups.

M is preferably selected from Groups 3 to 7 of the periodic table.

Groups R² to R¹¹ are preferably selected from the groups defined above in relation to the Formula I, II, III, IV, V and VI groups.

In this preferred embodiment of the present invention, D¹ and D² can be the same or different donor groups, for example oxygen, sulfur, an amine, an imine or a phosphine. Preferably D¹ and D² are selected from oxygen, sulfur, an amine of formula -N(R¹²)- or a phosphine of formula -P(R¹³)- wherein R¹² and R¹³ are hydrogen or (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), (vii) hydrocarbyl-substituted heteroatom groups and

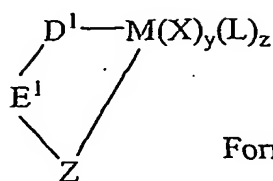
(viii) further imidazole-containing groups.

Preferably D^1 is nitrogen for example $-NR^1$ - or $=N$ - or a nitrogen-containing group, for example $-N(R^1)-R^{20}$ - wherein R^1 represents a monovalent group and R^{20} represents a divalent group derived from, for example, aliphatic hydrocarbon groups such as methyl, ethyl, ethylenyl, butyl, hexyl, isopropyl and tert-butyl. Examples of suitable alicyclic hydrocarbon groups are adamantyl, norbornyl, cyclopentyl and cyclohexyl. Examples of suitable aromatic hydrocarbon groups are phenyl, biphenyl, naphthyl, phenanthryl and anthryl. Examples of suitable alkyl substituted aromatic hydrocarbon groups are benzyl, tolyl, mesityl, 2,6-diisopropylphenyl and 2,4,6-triisopropyl. Examples of suitable heterocyclic groups are 2-pyridinyl, 3-pyridinyl, 2-thiophenyl, 2-furanyl, 2-pyrrolyl, 2-quinolinyl. Suitable substituents for forming heterosubstituted derivatives of said groups R^1 to R^{11} are, for example, chloro, bromo, fluoro, iodo, nitro, amino, cyano, ether, hydroxyl and silyl, methoxy, ethoxy, phenoxy (i.e. $-OC_6H_5$), tolyloxy (i.e. $-OC_6H_4(CH_3)$), xylyloxy, mesityloxy, dimethylamino, diethylamino, methylethylamino, thiomethyl, thiophenyl and trimethylsilyl. Examples of suitable heterosubstituted derivatives of said groups (i) to (v) are 2-chloroethyl, 2-bromocyclohexyl, 2-nitrophenyl, 4-ethoxyphenyl, 4-chloro-2-pyridinyl, 4-dimethylaminophenyl and 4-methylaminophenyl. Examples of suitable hydrocarbyl-substituted heteroatom groups are chloro, bromo, fluoro, iodo, nitro, amino, cyano, ether, hydroxyl and silyl, methoxy, ethoxy, phenoxy (i.e. $-OC_6H_5$), tolyloxy (i.e. $-OC_6H_4(CH_3)$), xylyloxy, mesityloxy, dimethylamino, diethylamino, methylethylamino, thiomethyl, thiophenyl and trimethylsilyl. Any of the substituents R^1 to R^{11} may be linked to form cyclic structures. Substituents R^2 to R^{11} may also suitably be inorganic groups such as fluoro, chloro, bromo, iodo, nitro, amino, cyano and hydroxyl

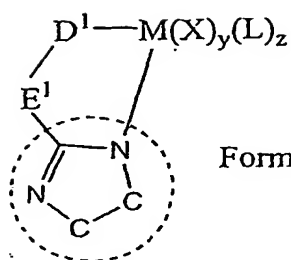
Preferably D^2 is a imidazole group selected from the groups of Formula Ia, IIa and IIIa above.

As indicated above, the values of m and n in the present invention are such that $m = n =$ zero or one. For the avoidance of doubt, this means that for a given complex, when m is zero, n is also zero. And when m is 1, n is also 1.

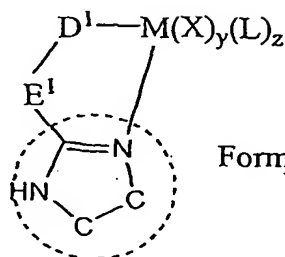
When m and n are zero in Formula A, the Formula reduces to Formula D, preferably to Formula E or Formula F



Formula D



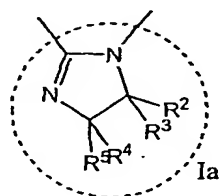
Formula E



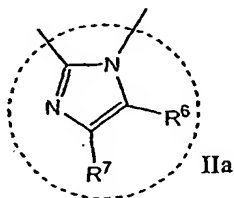
Formula F

wherein D¹, E¹, Z, M, X, L, y and z are as defined above, and wherein the imidazole nucleus within the dotted circle is selected from the divalent groups represented by the

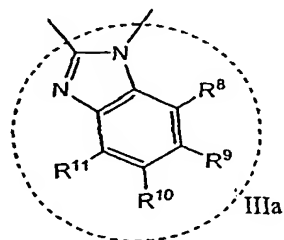
5 Formulae Ia, IIa, IIIa, IVa, Va and VIa



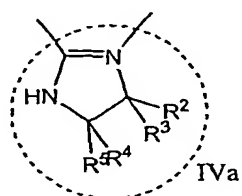
Ia



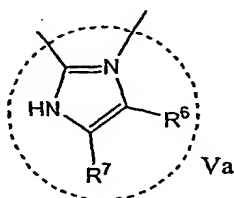
IIa



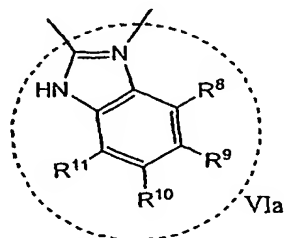
IIIa



IVa

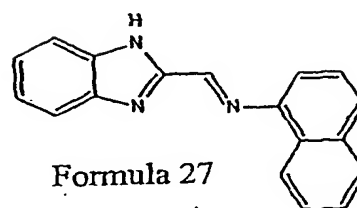
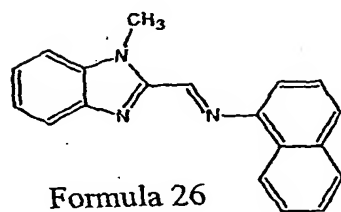
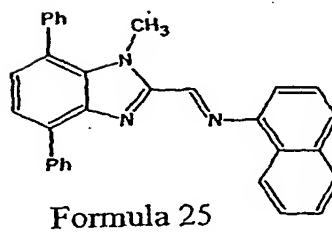
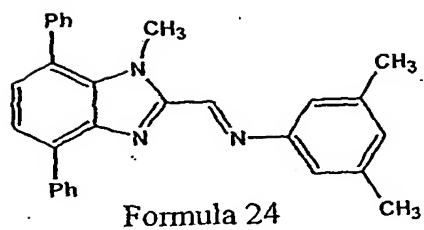
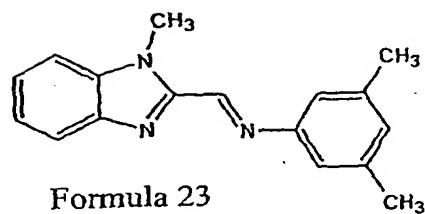
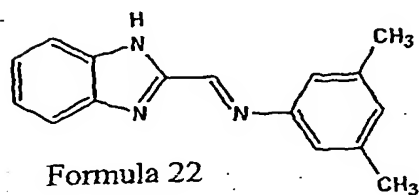
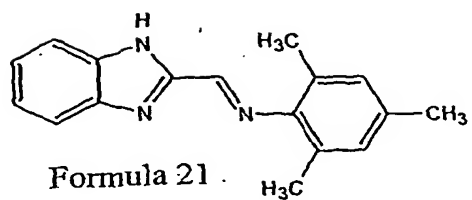
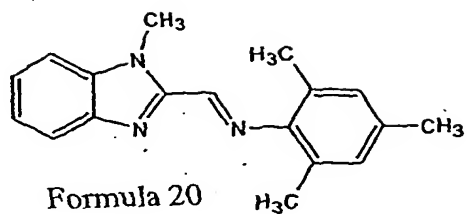


Va

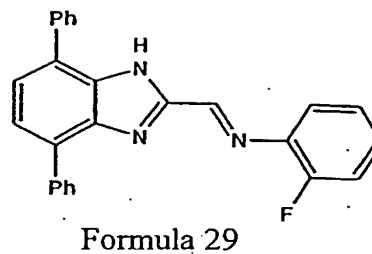
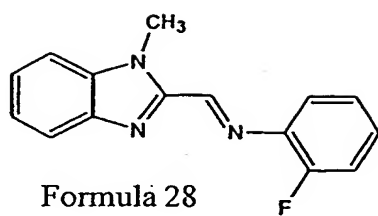


VIa

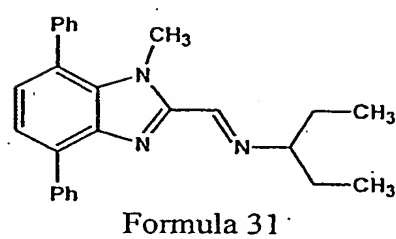
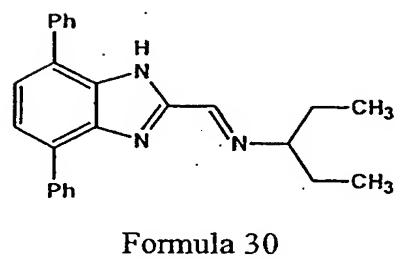
The following ligands represent some examples of those suitable for making the
10 complexes of Formula C and D in accordance with the present invention.



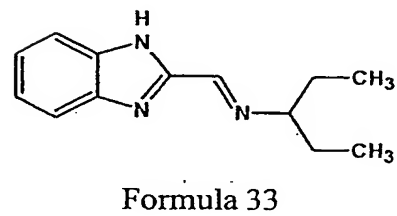
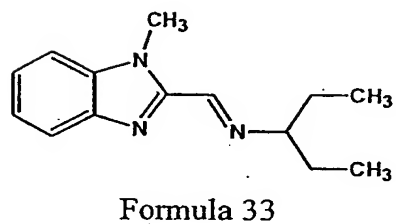
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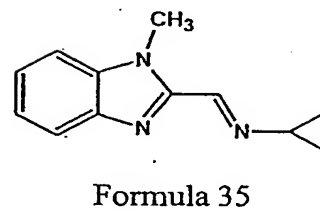
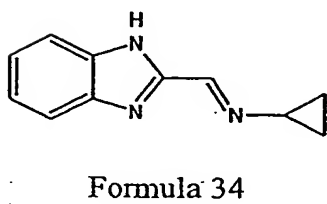


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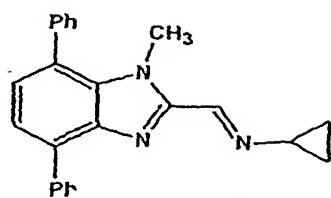


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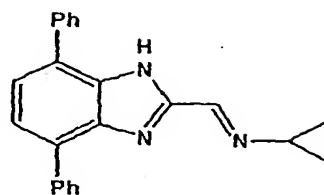
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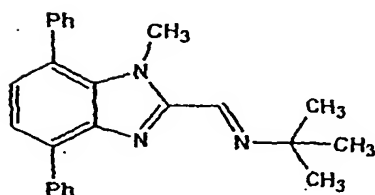
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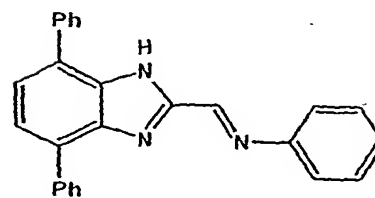
Formula 36



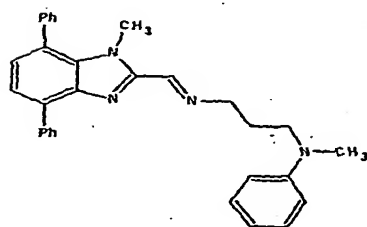
Formula 37



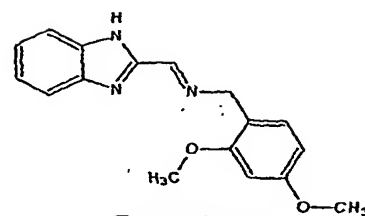
Formula 38



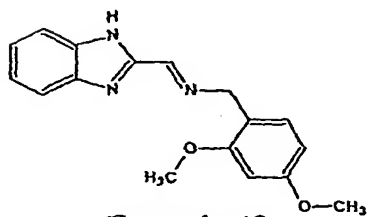
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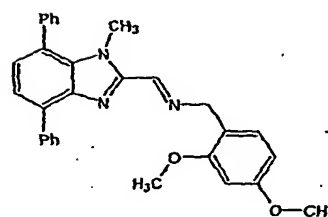
Formula 40



Formula 41

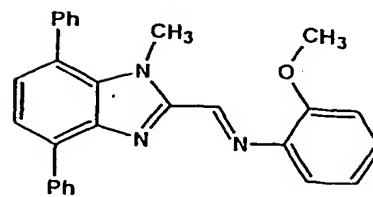
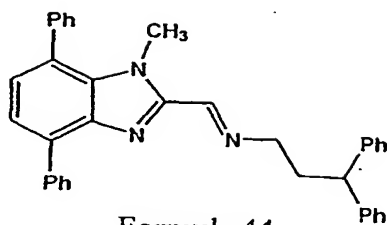


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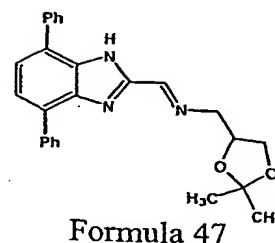
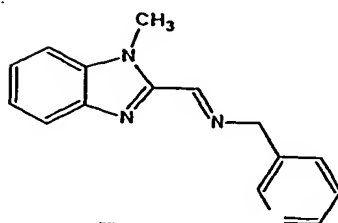


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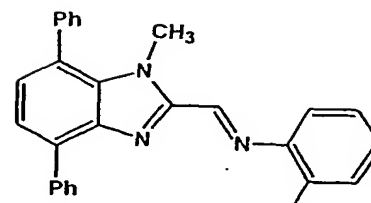
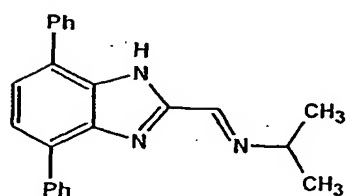
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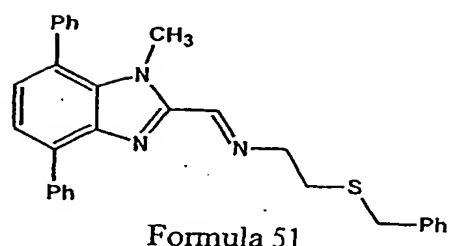
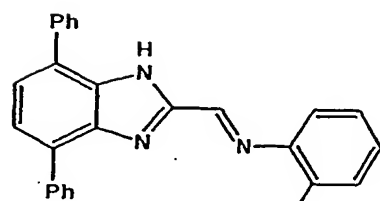
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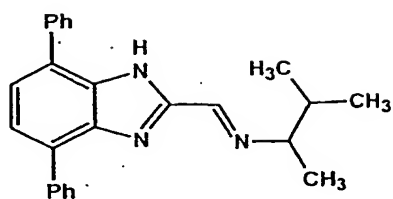


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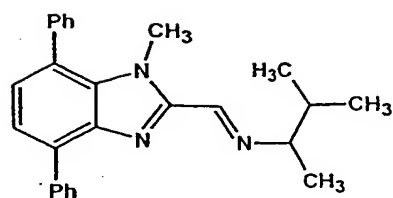


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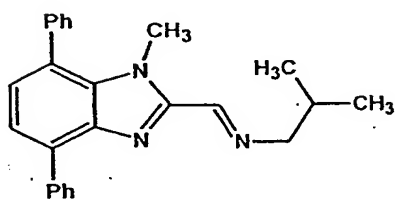
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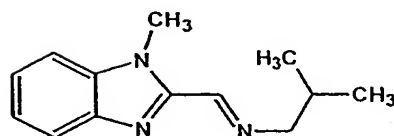
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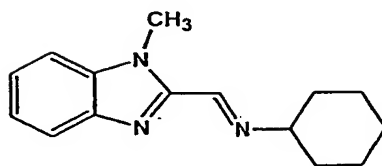
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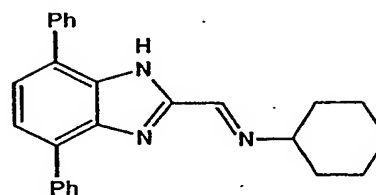
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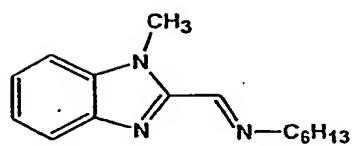
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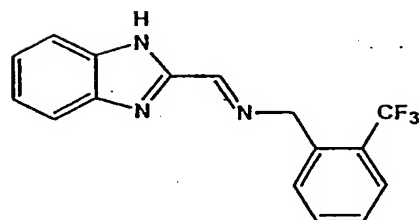
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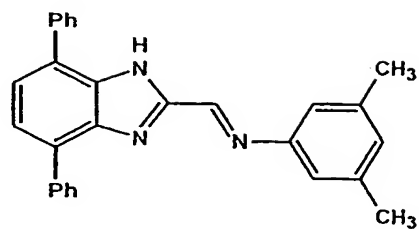
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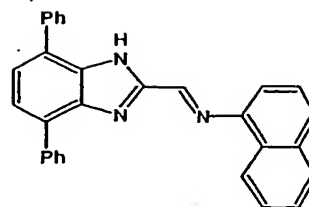
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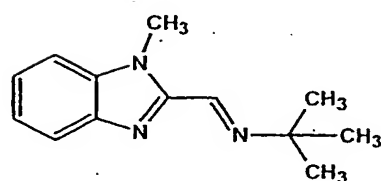
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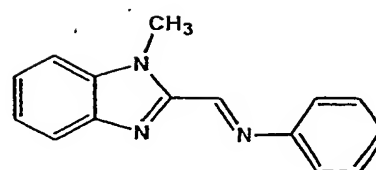
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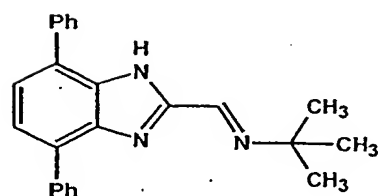
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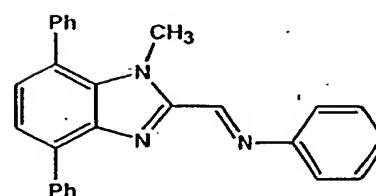
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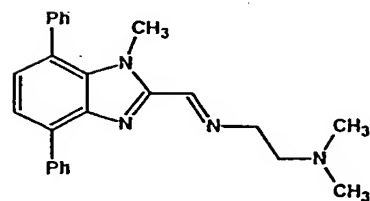
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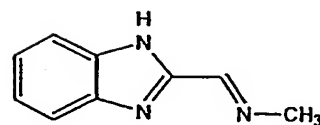
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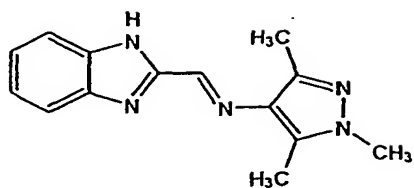
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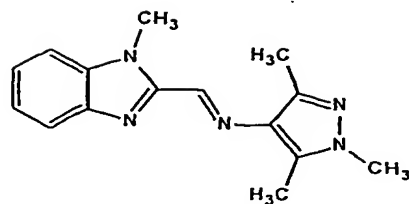
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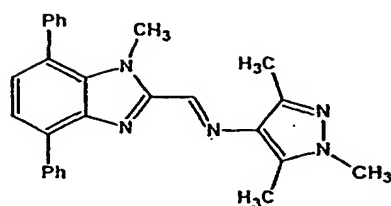
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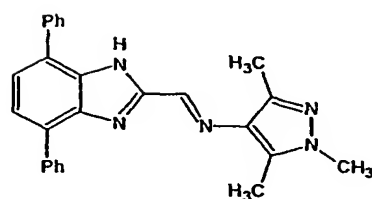
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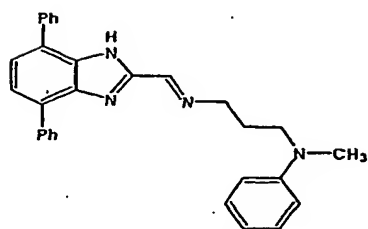
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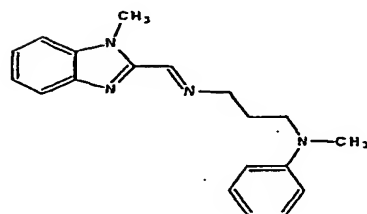
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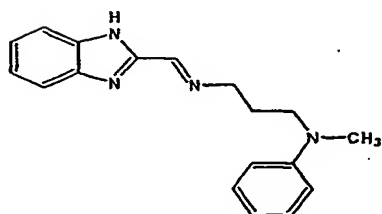
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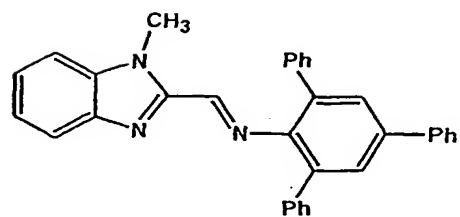
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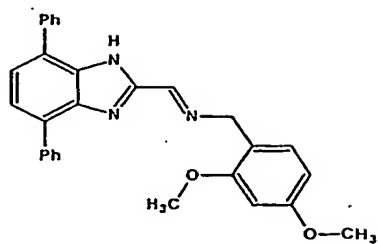
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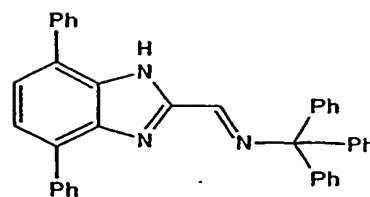
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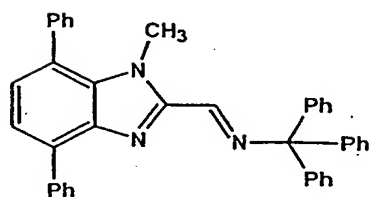
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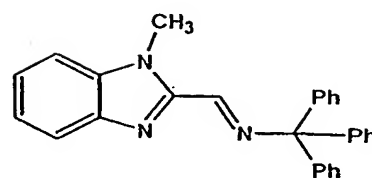
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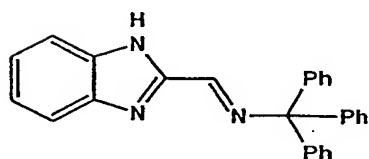
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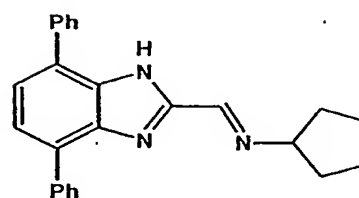
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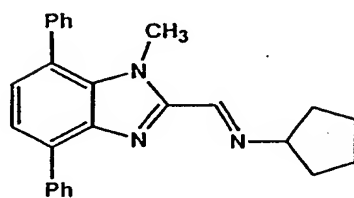
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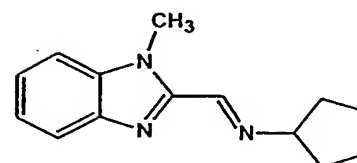
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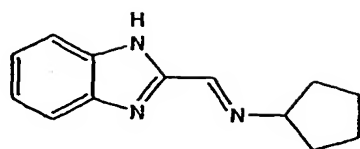
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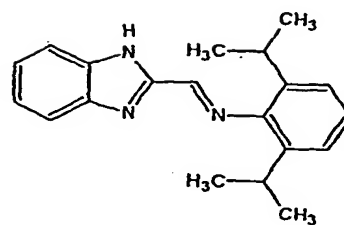
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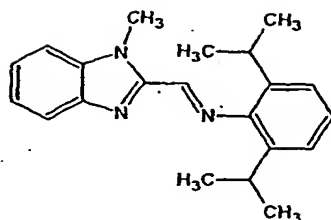
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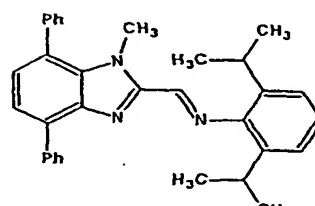
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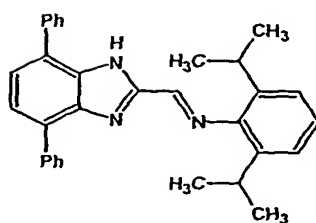
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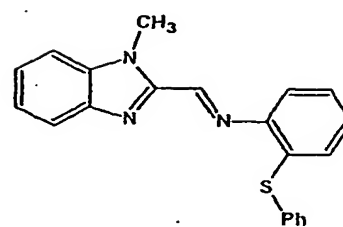
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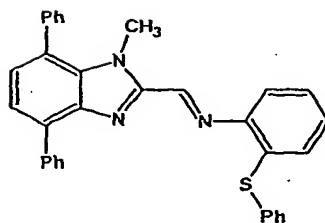
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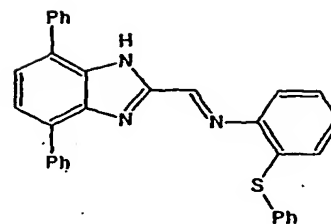
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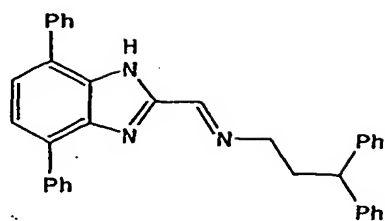


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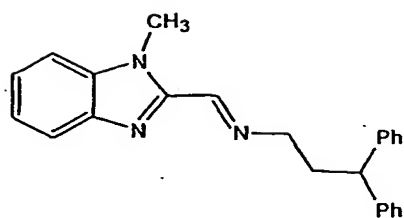


Formula 91

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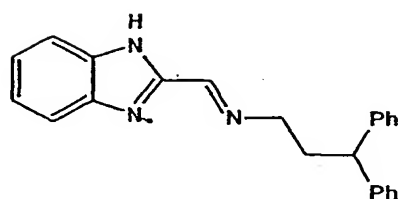


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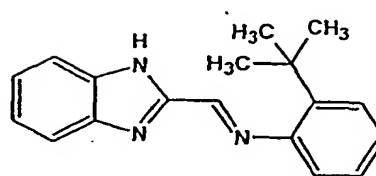


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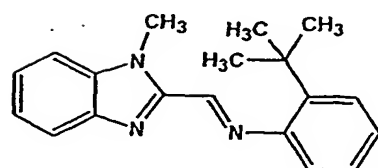


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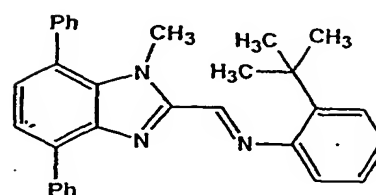


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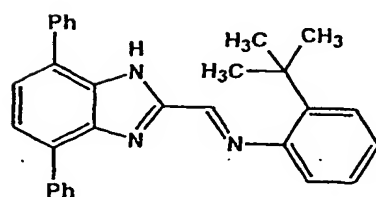


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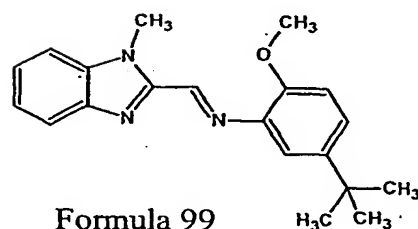


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Formula 98

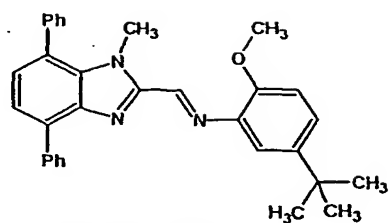


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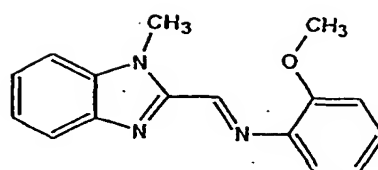
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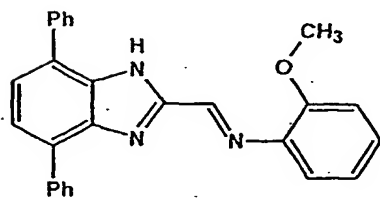


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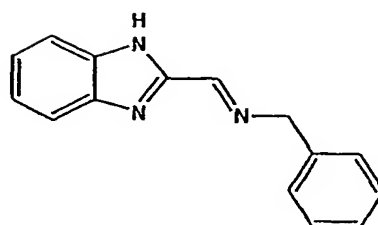


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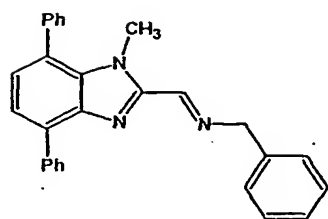


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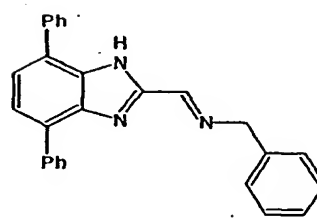


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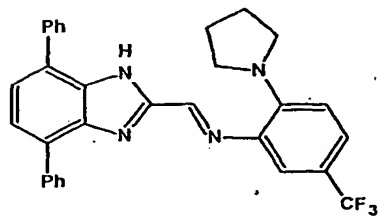


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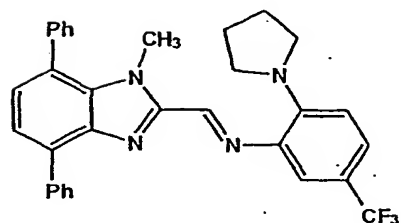


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Formula 106

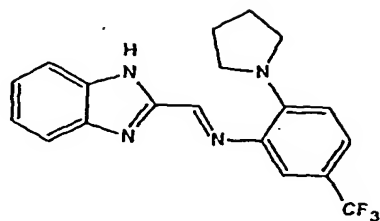


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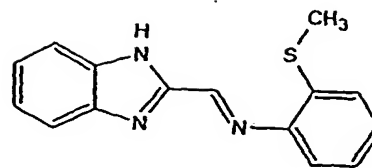
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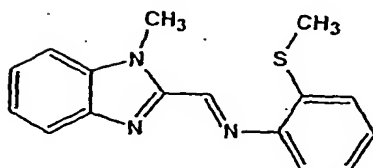


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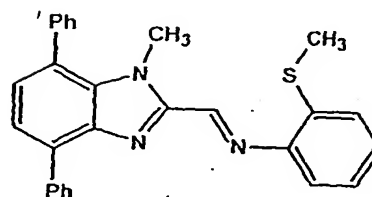


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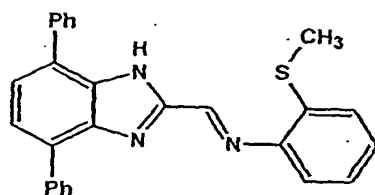


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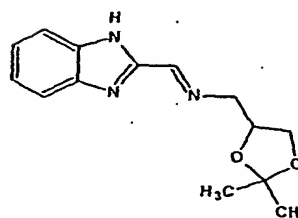


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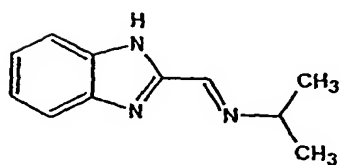


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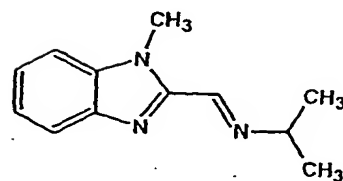


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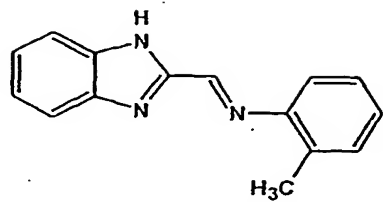


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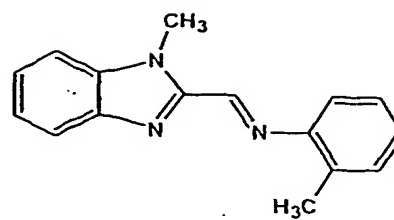


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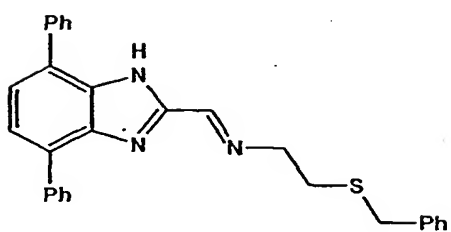
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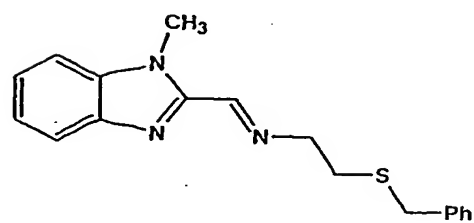
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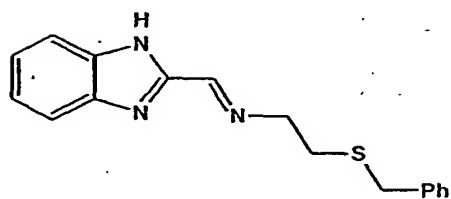
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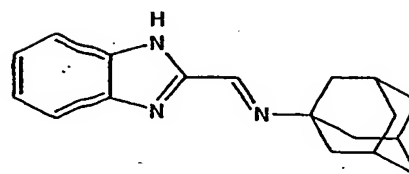
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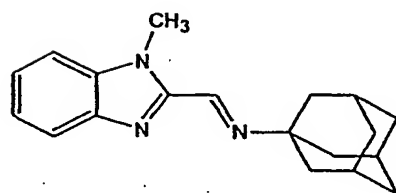
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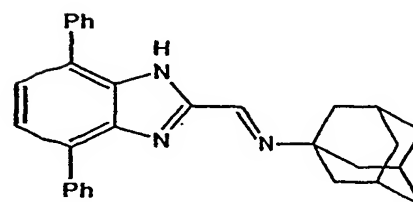
Formula 120



Formula 121

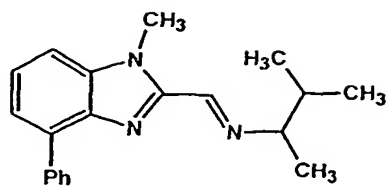


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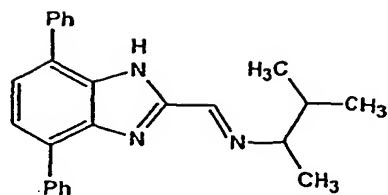


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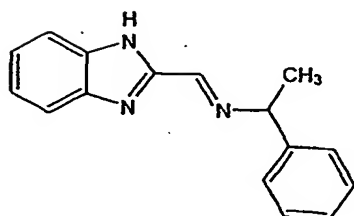


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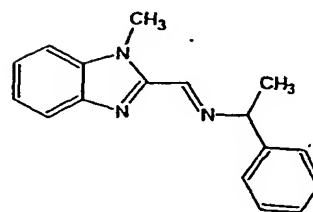


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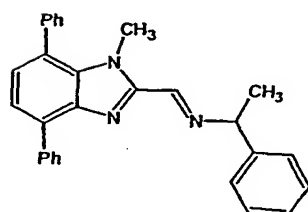


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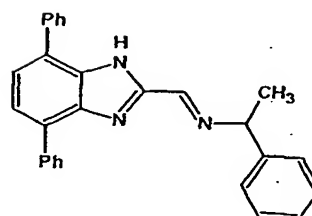


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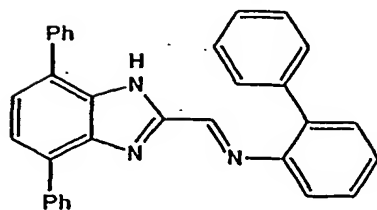


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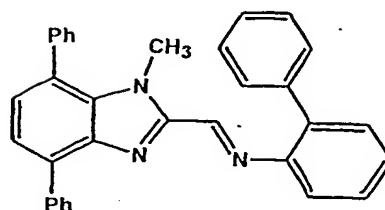


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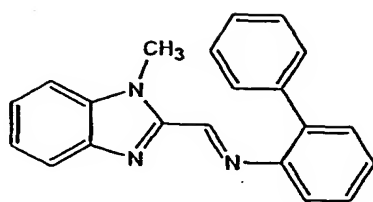
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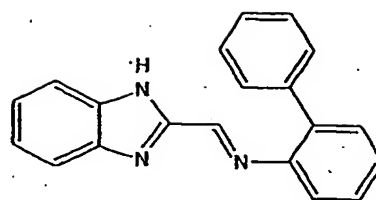
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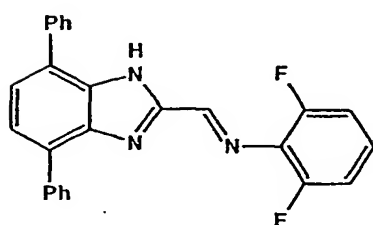


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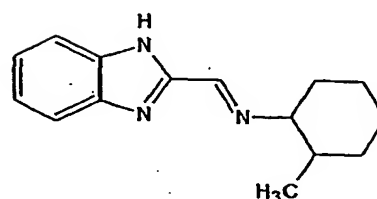


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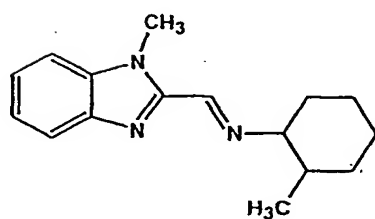


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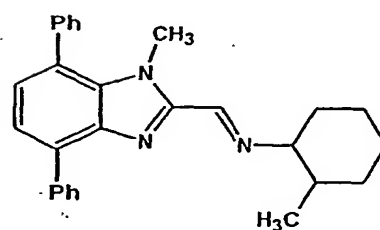


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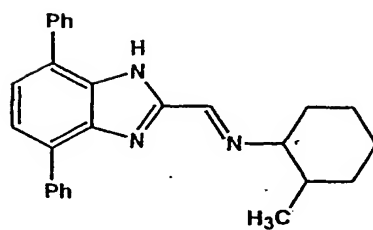


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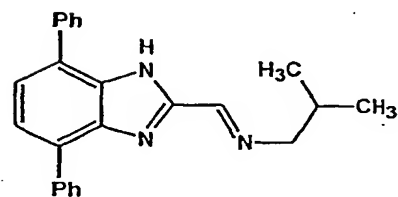


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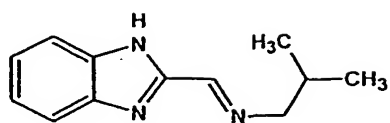
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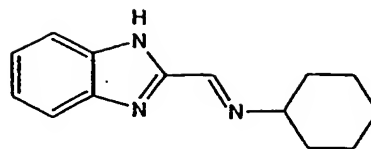
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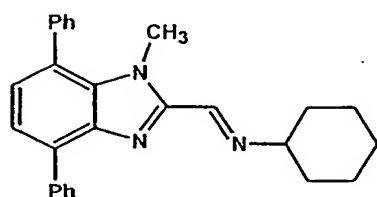
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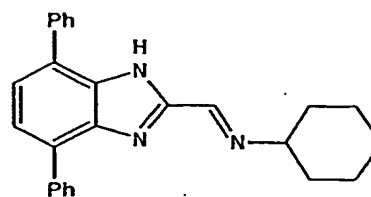
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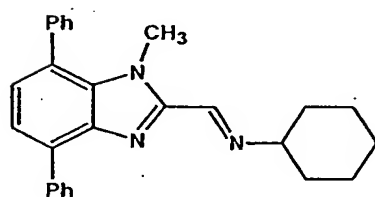
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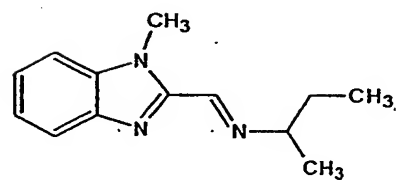
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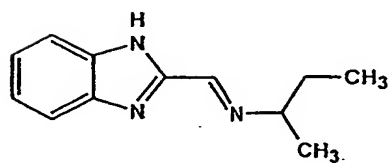
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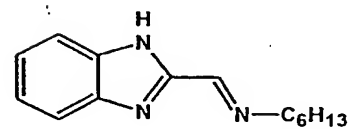
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Formula 145



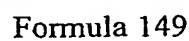
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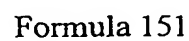
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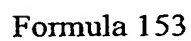
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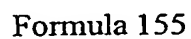
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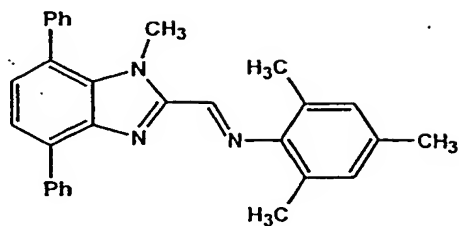


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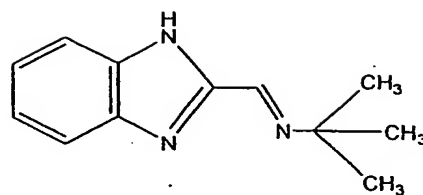


Formula 154





Formula 156

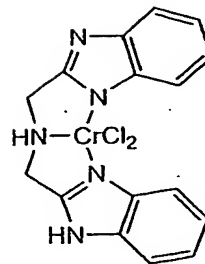
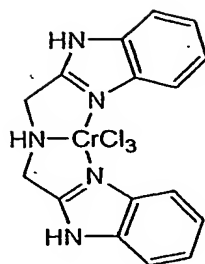
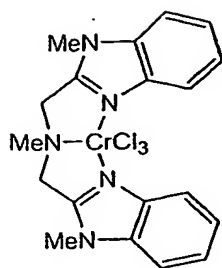


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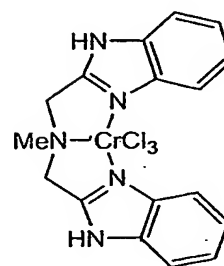
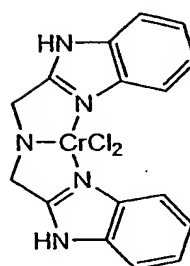
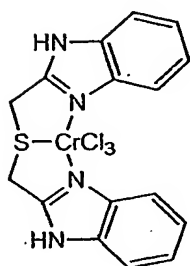
These ligands can be used to make complexes and catalysts in accordance with the present invention wherein the transition metal is preferably titanium, zirconium, hafnium, vanadium or chromium.

The following are examples of transition metal complexes that can be employed in the catalyst of the present invention: -

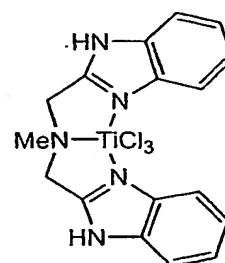
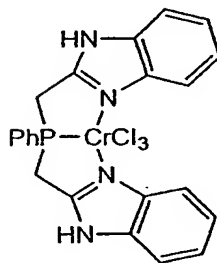
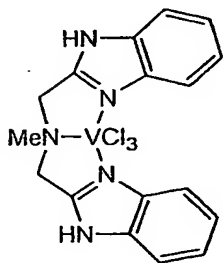
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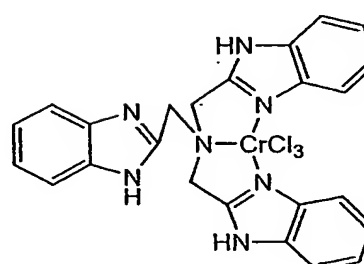
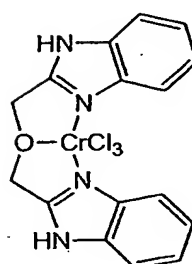
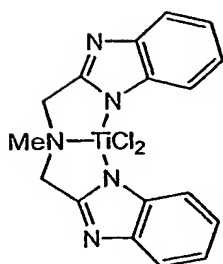
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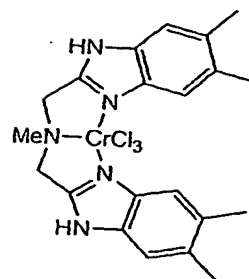
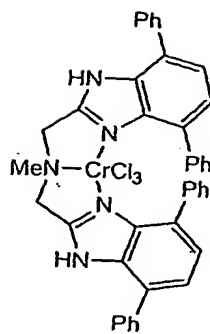
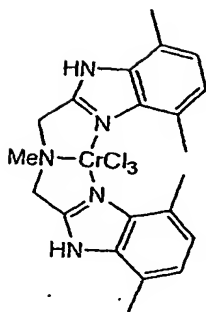
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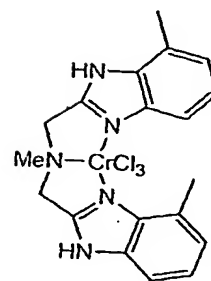
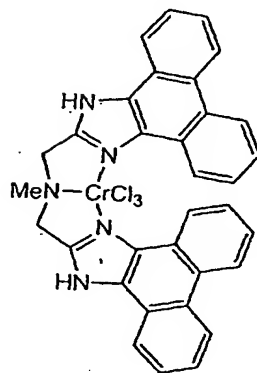
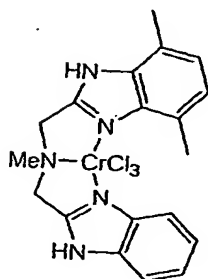
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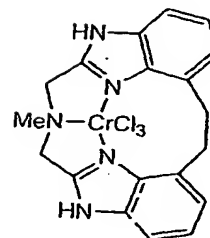
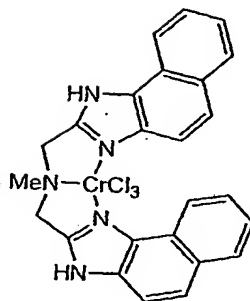
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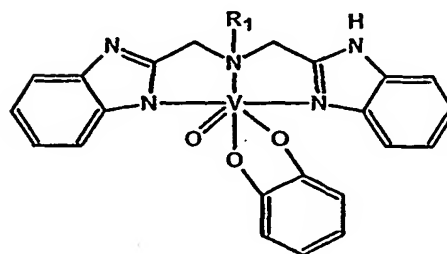
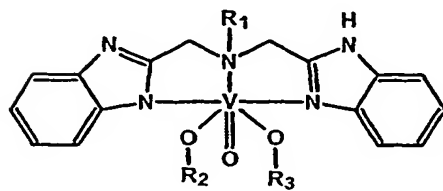
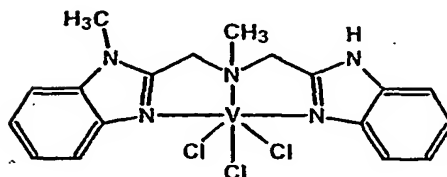
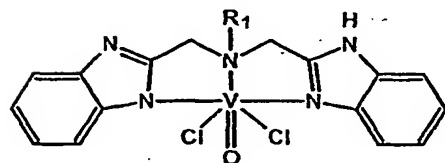
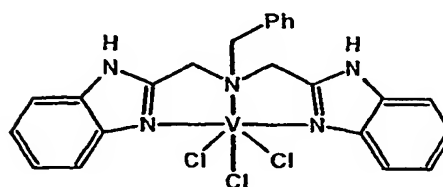
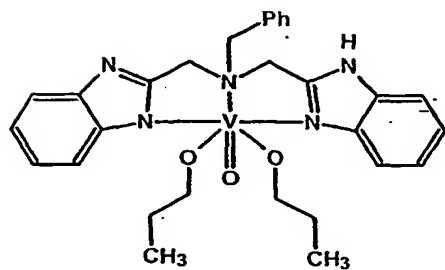
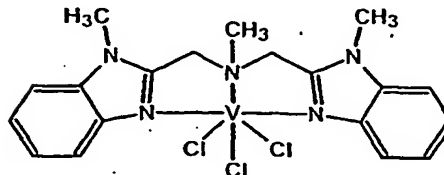
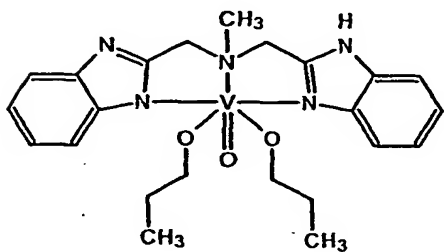
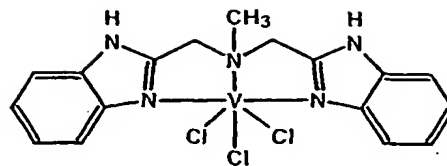
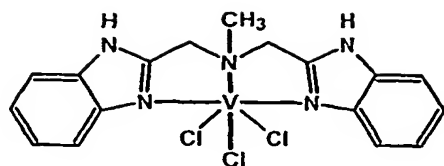
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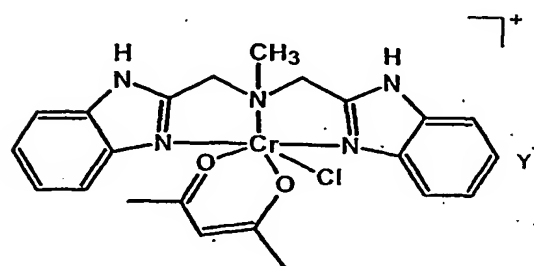
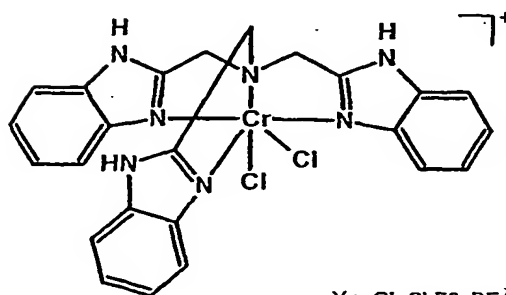
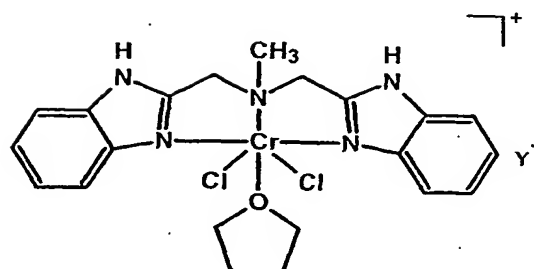
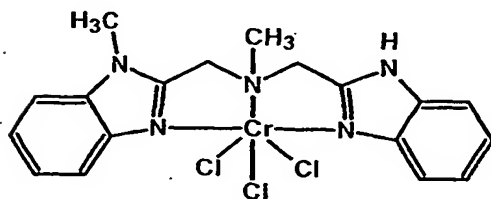
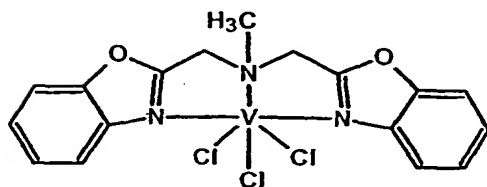
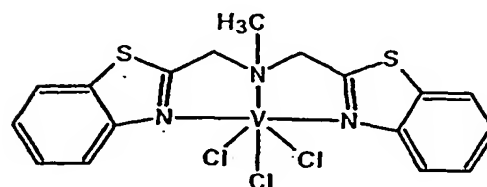
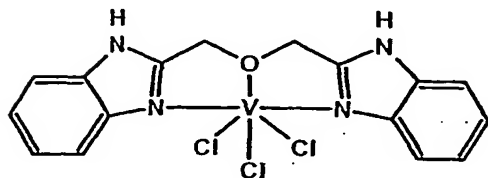
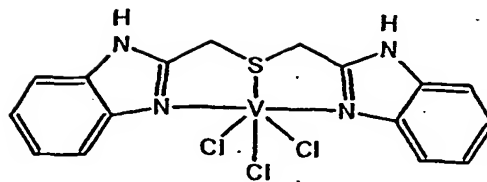
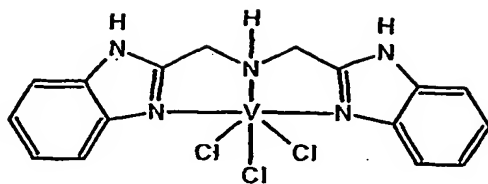
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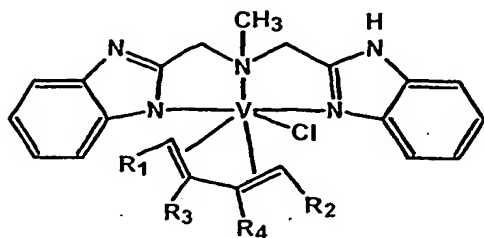


R₁-R₃ = alkyl, aryl, etc.

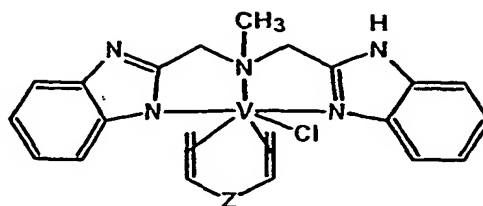


Y = Cl, SbF₆, BF₄, B(C₆F₅)₄, etc

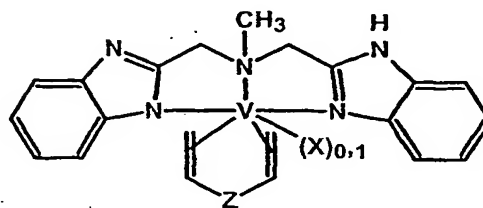
The following Formulae illustrate the transition metal compounds according to the present invention wherein L is a diene:



R₁ - R₄ = alkyl, aryl, etc.



Z = divalent organic or inorganic radical as -CH₂-, -O-, etc.



Z = divalent organic or inorganic radical as -CH₂-, -O-, etc.

X = Cl, Br, I, NMe₂, OR, SR, etc.

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The catalyst of the present invention can, if desired, be utilised on a support material. Suitable support materials are, for example, silica, alumina, or zirconia, magnesia, magnesium chloride or a polymer or prepolymer, for example polyethylene, polystyrene, or poly(aminostyrene).

5 The catalysts of the present invention can if desired comprise more than one of the defined transition metal compounds.

 In addition to said one or more defined transition metal compounds, the catalysts of the present invention can also include one or more other catalysts for polymerising 1-olefins. Preferably such catalysts are other types of transition metal compounds or
10 catalysts, for example, transition metal compounds of the type used in conventional Ziegler-Natta catalyst systems, metallocene-based catalysts, or heat activated supported chromium oxide catalysts (eg Phillips-type catalyst). The catalysts of the present invention may also be used in conjunction with other catalysts producing only 1-olefins, either inside or outside the polymerisation reactor, and in this way make copolymers of
15 ethylene or propylene and these 1-olefins. Suitable catalysts for producing 1-olefins may produce only 1-butene, only 1-hexene or a distribution (for example, a Schulz-Flory distribution) of 1-olefins.

 If desired the catalysts can be formed in situ in the presence of the support material, or the support material can be pre-impregnated or premixed, simultaneously or
20 sequentially, with one or more of the catalyst components. The catalysts of the present invention can if desired be supported on a heterogeneous catalyst, for example, a magnesium halide supported Ziegler Natta catalyst, a Phillips type (chromium oxide) supported catalyst or a supported metallocene catalyst. Formation of the supported catalyst can be achieved for example by treating the transition metal compounds of the
25 present invention with alumoxane in a suitable inert diluent, for example a volatile hydrocarbon, slurring a particulate support material with the product and evaporating the volatile diluent. The produced supported catalyst is preferably in the form of a free-flowing powder. The quantity of support material employed can vary widely, for example from 100,000 to 1 grams per gram of metal present in the transition metal
30 compound.

 The present invention further provides a process for the polymerisation and copolymerisation of 1-olefins, cycloolefins or dienes, comprising contacting the

monomer under polymerisation conditions with the polymerisation catalyst of the present invention.

Suitable monomers for use in making homopolymers using the polymerisation process of the present invention are, for example, ethylene, propylene, butene, hexene, styrene or conjugated or non-conjugated dienes. Preferred monomers are ethylene and propylene.

Suitable monomers for use in making copolymers using the polymerisation process of the present invention are ethylene, propylene, 1-butene, 1-hexene, 4-methylpentene-1, 1-octene, norbornene, substituted norbornenes, dienes, eg butadiene, ethylidene norbornene, methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, vinyl chloride, and styrene.

A particularly preferred process in accordance with the present invention is the copolymerisation of ethylene and or propylene with comonomers selected from 1-olefins, acrylic acid esters, vinyl esters and vinyl aromatic compounds. Examples of suitable comonomers are 1-butene, 1-hexene, 4-methylpentene-1, methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, and styrene.

Preferred polymerisation processes are the homopolymerisation of ethylene or the homopolymerisation of propylene or copolymerisation of ethylene with one or more of propylene, butene, hexene-1 and 4-methylpentene-1 or copolymerisation of propylene with one or more of ethylene or butene.

The polymerisation conditions can be, for example, bulk phase, solution phase, slurry phase or gas phase. If desired, the catalyst can be used to polymerise ethylene under high pressure/high temperature process conditions wherein the polymeric material forms as a melt in supercritical ethylene. Preferably the polymerisation is conducted under gas phase fluidised or stirred bed conditions.

Slurry phase polymerisation conditions or gas phase polymerisation conditions are particularly useful for the production of high-density grades of polyethylene. In these processes the polymerisation conditions can be batch, continuous or semi-continuous. In the slurry phase process and the gas phase process, the catalyst is generally fed to the polymerisation zone in the form of a particulate solid. This solid can be, for example, an undiluted solid catalyst system formed from the complex A and an activator, or can be the solid complex A alone. In the latter situation, the activator

can be fed to the polymerisation zone, for example as a solution, separately from or together with the solid complex. Preferably the catalyst system or the transition metal complex component of the catalyst system employed in the slurry polymerisation and gas phase polymerisation is supported on a support material. Most preferably the catalyst system is supported on a support material prior to its introduction into the polymerisation zone. Suitable support materials are, for example, silica, alumina, zirconia, talc, kieselguhr, magnesia, magnesium chloride and polymers. Impregnation of the support material can be carried out by conventional techniques, for example, by forming a solution or suspension of the catalyst components in a suitable diluent or solvent, and slurring the support material therewith. The support material thus impregnated with catalyst can then be separated from the diluent for example, by filtration or evaporation techniques.

In the slurry phase polymerisation process the solid particles of catalyst, or supported catalyst, are fed to a polymerisation zone either as dry powder or as a slurry in the polymerisation diluent. Preferably the particles are fed to a polymerisation zone as a suspension in the polymerisation diluent. The polymerisation zone can be, for example, an autoclave or similar reaction vessel, or a continuous loop reactor, e.g. of the type well known in the manufacture of polyethylene by the Phillips Process. When the polymerisation process of the present invention is carried out under slurry conditions the polymerisation is preferably carried out at a temperature above 0°C, most preferably above 15°C. The polymerisation temperature is preferably maintained below the temperature at which the polymer commences to soften or sinter in the presence of the polymerisation diluent. If the temperature is allowed to go above the latter temperature, fouling of the reactor can occur. Adjustment of the polymerisation within these defined temperature ranges can provide a useful means of controlling the average molecular weight of the produced polymer. A further useful means of controlling the molecular weight is to conduct the polymerisation in the presence of hydrogen gas which acts as chain transfer agent. Generally, the higher the concentration of hydrogen employed, the lower the average molecular weight of the produced polymer.

The use of hydrogen gas as a means of controlling the average molecular weight of the polymer or copolymer applies generally to the polymerisation process of the present invention. For example, hydrogen can be used to reduce the average molecular

weight of polymers or copolymers prepared using gas phase, slurry phase or solution phase polymerisation conditions. The quantity of hydrogen gas to be employed to give the desired average molecular weight can be determined by simple "trial and error" polymerisation tests.

5 Methods for operating gas phase polymerisation processes are well known in the art. Such methods generally involve agitating (e.g. by stirring, vibrating or fluidising) a bed of catalyst, or a bed of the target polymer (i.e. polymer having the same or similar physical properties to that which it is desired to make in the polymerisation process) containing a catalyst, and feeding thereto a stream of monomer at least partially in the
10 gaseous phase, under conditions such that at least part of the monomer polymerises in contact with the catalyst in the bed. The bed is generally cooled by the addition of cool gas (eg recycled gaseous monomer) and/or volatile liquid (eg a volatile inert hydrocarbon, or gaseous monomer which has been condensed to form a liquid). The polymer produced in, and isolated from, gas phase processes forms directly a solid in the
15 polymerisation zone and is free from, or substantially free from liquid. As is well known to those skilled in the art, if any liquid is allowed to enter the polymerisation zone of a gas phase polymerisation process the quantity of liquid is small in relation to the quantity of polymer present in the polymerisation zone. This is in contrast to
20 "solution phase" processes wherein the polymer is formed dissolved in a solvent, and "slurry phase" processes wherein the polymer forms as a suspension in a liquid diluent.

 The gas phase process can be operated under batch, semi-batch, or so-called "continuous" conditions. It is preferred to operate under conditions such that monomer is continuously recycled to an agitated polymerisation zone containing polymerisation catalyst, make-up monomer being provided to replace polymerised monomer, and
25 continuously or intermittently withdrawing produced polymer from the polymerisation zone at a rate comparable to the rate of formation of the polymer, fresh catalyst being added to the polymerisation zone to replace the catalyst withdrawn from the polymerisation zone with the produced polymer.

 When using the catalysts of the present invention under gas phase
30 polymerisation conditions, the catalyst, or one or more of the components employed to form the catalyst can, for example, be introduced into the polymerisation reaction zone in liquid form, for example, as a solution in an inert liquid diluent. Thus, for example,

the transition metal component, or the activator component, or both of these components can be dissolved or slurried in a liquid diluent and fed to the polymerisation zone. Under these circumstances it is preferred the liquid containing the component(s) is sprayed as fine droplets into the polymerisation zone. The droplet diameter is preferably within the range 1 to 1000 microns. EP-A-0593083, the teaching of which is hereby incorporated into this specification, discloses a process for introducing a polymerisation catalyst into a gas phase polymerisation. The methods disclosed in EP-A-0593083 can be suitably employed in the polymerisation process of the present invention if desired.

The present invention also provides a process for the oligomerisation and cooligomerisation of 1-olefins, comprising contacting the monomeric olefin under oligomerisation conditions with the catalyst of the present invention.

Suitable monomers for use in making homooligomers using the oligomerisation process of the of the present invention are, for example, ethylene, propylene, butene, hexene, and styrene. The preferred monomer is ethylene.

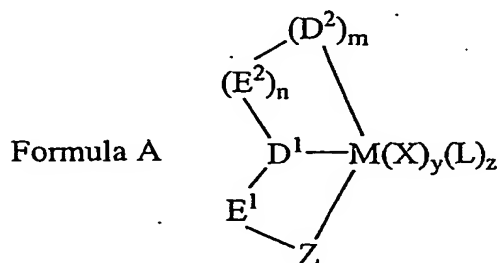
Suitable monomers for use in making co-oligomers using the oligomerisation process of the present invention are ethylene, propylene, 1-butene, 1-hexene, 1-octene, 1-decene, 1-dodecene and further 1-olefins of the series $C(n)H(2n)$ where n is an integer.

There exist a number of options for the oligomerisation reactor including batch, semi-batch, and continuous operation. The oligomerisation and co-oligomerisation reactions of the present invention can be performed under a range of process conditions that are readily apparent to those skilled in the art: as a homogeneous liquid phase reaction in the presence or absence of an inert hydrocarbon diluent such as toluene or heptanes; as a two-phase liquid/liquid reaction; as a slurry process where the catalyst is in a form that displays little or no solubility; as a bulk process in which essentially neat reactant and/or product olefins serve as the dominant medium; as a gas-phase process in which at least a portion of the reactant or product olefin(s) are transported to or from a supported form of the catalyst via the gaseous state. Evaporative cooling from one or more monomers or inert volatile liquids is but one method that can be employed to effect the removal of heat from the reaction. The (co-)oligomerisation reactions may be performed in the known types of gas-phase reactors, such as circulating bed, vertically or horizontally stirred-bed, fixed-bed, or fluidised-bed reactors, liquid-phase reactors,

such as plug-flow, continuously stirred tank, or loop reactors, or combinations thereof. A wide range of methods for effecting product, reactant, and catalyst separation and/or purification are known to those skilled in the art and may be employed: distillation, filtration, liquid-liquid separation, slurry settling, extraction, etc. One or more of these methods may be performed separately from the (co-)oligomerisation reaction or it may be advantageous to integrate at least some with a (co-)oligomerisation reaction; a non-limiting example of this would be a process employing catalytic (or reactive) distillation. Also advantageous may be a process which includes more than one reactor, a catalyst kill system between reactors or after the final reactor, or an integrated reactor/separator/purifier. While all catalyst components, reactants, inerts, and products could be employed in the present invention on a once-through basis, it is often economically advantageous to recycle one or more of these materials; in the case of the catalyst system, this might require reconstituting one or more of the catalyst components to achieve the active catalyst system. It is within the scope of this invention that a (co)oligomerisation product might also serve as a reactant (e.g. 1-hexene, produced via the oligomerisation of ethylene, might be converted to decene products via a subsequent co-oligomerisation reaction with two further ethylene units).

The catalyst systems of the present invention can present a variety of advantages over the prior art systems. In general the catalysts are easy to synthesise, have high activity and good catalyst life when employed under conventional industrial polymerisation conditions. Generally the catalysts exhibit single site behaviour which tends to favour the production of narrow molecular weight distribution polymers having uniform properties. Generally, the vanadium based catalysts of the present invention are capable of making very high molecular weight polymers.

A further aspect of the present invention provides a novel transition metal compound having the Formula A

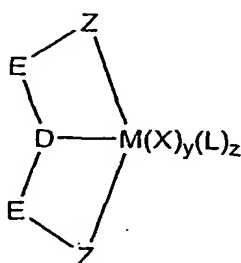


wherein Z comprises a five-membered heterocyclic group, the five membered heterocyclic group containing at least one carbon atom, at least one nitrogen atom and at least one other hetero atom selected from nitrogen, sulphur and oxygen, the remaining atoms in said ring being selected from nitrogen and carbon; M is a metal from Group 3 to 11 of the Periodic Table or a lanthanide metal; E^1 and E^2 are divalent groups independently selected from (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups and (vi) heterosubstituted derivatives of said groups (i) to (v); D^1 and D^2 are donor atoms or groups; X is an anionic group, L is a neutral donor group; $n = m =$ zero or 1; y and z are independently zero or integers such that the number of X and L groups satisfy the valency and oxidation state of the metal M.

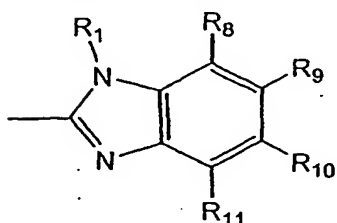
M is preferably selected from Groups 3 to 7 of the periodic table.

The preferences set out above in relation to the transition metal complex component of the catalyst of the present invention apply equally to the novel transition metal compound *per se* of the present invention

A preferred novel transition metal compound in accordance with the present has the Formula



Z is specifically an imidazole-containing group of formula:



wherein R_1 , R_8 , R_9 , R_{10} and R_{11} are independently hydrogen or a monovalent (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), and (vii) hydrocarbyl-substituted heteroatom groups. These defined groups preferably contain 1 to 30, more preferably 2 to 20, most preferably 2 to 12 carbon atoms. Examples of suitable aliphatic hydrocarbon groups are methyl, ethyl, ethylenyl, butyl, hexyl, isopropyl and tert-butyl. Examples of suitable alicyclic hydrocarbon groups are adamantyl, norbornyl, cyclopentyl and cyclohexyl. Examples of suitable aromatic hydrocarbon groups are phenyl, biphenyl, naphthyl, phenanthryl and anthryl. Examples of suitable alkyl substituted aromatic hydrocarbon groups are benzyl, tolyl, mesityl, 2,6-diisopropylphenyl and 2,4,6-triisopropyl. Examples of suitable heterocyclic groups are 2-pyridinyl, 3-pyridinyl, 2-thiophenyl, 2-furanyl, 2-pyrrolyl, 2-quinolinyl. Suitable substituents for forming heterosubstituted derivatives of said groups R_1 to R_{11} are, for example, chloro, bromo, fluoro, iodo, nitro, amino, cyano, ether, hydroxyl and silyl, methoxy, ethoxy, phenoxy (i.e. $-\text{OC}_6\text{H}_5$), tolyloxy (i.e. $-\text{OC}_6\text{H}_4(\text{CH}_3)$), xilyloxy, mesityloxy, dimethylamino, diethylamino, methylethylamino, thiomethyl, thiophenyl and trimethylsilyl. Examples of suitable heterosubstituted derivatives of said groups (i) to (v) are 2-chloroethyl, 2-bromocyclohexyl, 2-nitrophenyl, 4-ethoxyphenyl, 4-chloro-2-pyridinyl, 4-dimethylaminophenyl and 4-methylaminophenyl. Examples of suitable hydrocarbyl-substituted heteroatom groups are chloro, bromo, fluoro, iodo, nitro, amino, cyano, ether, hydroxyl and silyl, methoxy, ethoxy, phenoxy (i.e. $-\text{OC}_6\text{H}_5$), tolyloxy (i.e. $-\text{OC}_6\text{H}_4(\text{CH}_3)$), xilyloxy, mesityloxy, dimethylamino, diethylamino, methylethylamino, thiomethyl, thiophenyl and trimethylsilyl. Any of the substituents R_1 to R_{11} may be linked to form cyclic structures. Substituents R_2 to R_{11} may also suitably be inorganic groups such as fluoro, chloro, bromo, iodo, nitro, amino, cyano and hydroxyl.

Further suitable imidazole-containing groups may be obtained by removal of substituent R_1 , for example by deprotonation when R_1 is hydrogen, to give formally monoanionic imidazole-containing groups.

R_1 is preferably hydrogen, an aliphatic hydrocarbon group, an aromatic hydrocarbon group or is removed to give a formally monoanionic benzimidazole group. R_8 to R_{11} are preferably hydrogen, an aliphatic hydrocarbon group or an aromatic

hydrocarbon group.

M is preferably a metal selected from Groups 3 to 11 of the periodic table, more preferably selected from Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn and most preferably V and Cr.

- 5 E is independently selected from divalent (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), and (vii) hydrocarbyl-substituted heteroatom groups. Examples of suitable divalent group R_5 are $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, 1,2-phenylene, *trans*-1,2-cyclopentane, *trans*-1,2-
10 cyclohexane, 2,3-butane, 1,1'-biphenyl, 1,1'-binaphthyl, and $-Si(Me)_2-$. It is preferred that E is an aliphatic or aromatic hydrocarbon group. More preferably E is $-CH_2-$.

- D is a donor group, for example oxygen, sulfur, an amine, an imine or a phosphine. Preferably D is oxygen, sulfur, an amine of formula $-N(R_{12})-$ or a phosphine of formula $-P(R_{13})-$ wherein R_{12} and R_{13} are hydrogen or (i) aliphatic hydrocarbon, (ii)
15 alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), (vii) hydrocarbyl-substituted heteroatom groups and (viii) further imidazole-containing groups. Alternatively R_{12} or R_{13} may be removed, for example by deprotonation when they are hydrogen, to give a formally monoanionic fragments.
20 More preferably D is an amine of formula $-N(R_{12})-$ as define above. R_{12} is preferably hydrogen, an aliphatic hydrocarbon, an aromatic hydrocarbon or a further imidazole containing group.

- X is an anionic group and can be, for example, a halide, preferably chloride or bromide; or a hydrocarbyl group, for example, methyl, benzyl or phenyl; a carboxylate,
25 for example, acetate or acetylacetate; an oxide; an amide, for example diethyl amide; an alkoxide, for example, methoxide, ethoxide or phenoxide. Alternatively, X can be a non-coordinating or weakly-coordinating anion, for example, tetrafluoroborate, a fluorinated aryl borate or a triflate. The anionic groups X may be the same or different and may independently be monoanionic, dianionic or trianionic.

- 30 L is a neutral donor group and can be, for example, a solvate molecule, for example diethyl ether or THF; an amine, for example, diethyl amine, trimethylamine or pyridine; a phosphine, for example trimethyl phosphine or triphenyl phosphine; or an

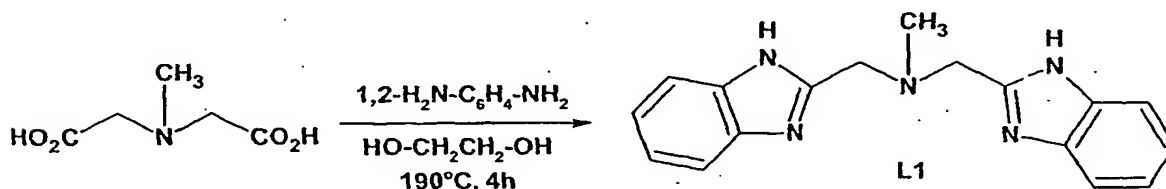
olefin, or a neutral, conjugated or nonconjugated diene, optionally substituted with one or more groups selected from hydrocarbyl or trimethylsilyl groups, said L having up to 40 carbon atoms and forming a π -complex with M.

Values y and z are independently zero or integers such that the number of X and L groups satisfy the valency and oxidation state of the metal M. The value of y depends on the formal charge on each group Z and D, the charge on the anionic group X and the oxidation state of the metal M. For example, if M is chromium in oxidation state +3, Z is a neutral groups and both D groups are neutral, then y is 3 if X is a monoanionic group (eg. chloride); if M is chromium in oxidation state +3, Z is a neutral group, one D group is monoanionic and the other D is neutral, then y is 2 if all X groups are monoanionic groups (e.g. chloride).

The invention is further illustrated with reference to the following Examples. In the Examples all manipulations of air/moisture-sensitive materials were performed on a conventional vacuum/inert atmosphere (nitrogen) line using standard Schlenk line techniques, or in an inert atmosphere glove box.

Example 1

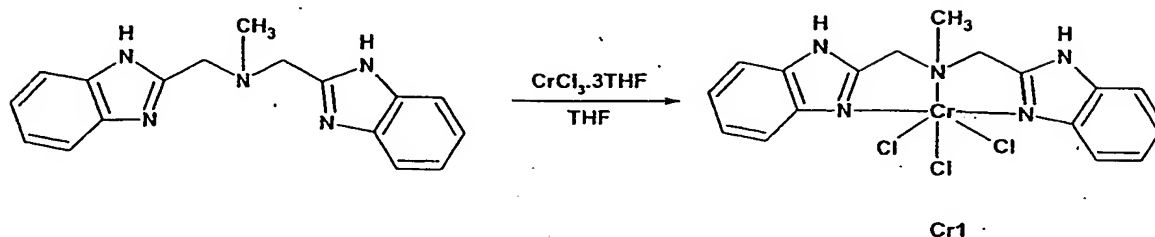
Preparation of N,N-bis(1H-benzimidazol-2-ylmethyl)-N-methylamine (L-1)



A mixture of 4.00 g (27.2 mmol) N-methyliminodiacetic acid and 5.99 g (54.4 mmol) o-phenylene diamine in 30 ml ethylene glycol was stirred at 190°C for 4 hours. The water produced during was distilled off continuously. At the end of the reaction, the reaction mixture was allowed to cool down to room temperature and then poured in 150 ml water. The obtained slurry was triturated for 30 min, filtered, washed with water (3 x 30 ml) and dried at 60°C under reduced pressure for 48 hours. Yield 6.88 g (87.0%). ¹H NMR (250 MHz, DMSO-d₆), δ 2.25 (s, 3H), 3.90 (s, 4H), 7.15 (m, 4H), 7.47-4.58 (m, 4H), 12.33 (br. s, 2H). Microanalysis, %: Calculated for C₁₇H₁₇N₅: C 70.10, H 5.84, N 24.05. Found: C 70.22, H 6.05, N 23.76. +CI MS (m/z): [292]. (+CI-MS is Positive Chemical Ionisation Mass Spectroscopy).

Example 2

Preparation of [N,N-bis(1H-benzimidazol-2-ylmethyl)-N-methylamine]trichlorochromium(III) (Cr-1)



- 5 A slurry of 0.50 g (1.72 mmol) L-1 and 0.64 g (1.72 mmol) $\text{CrCl}_3(\text{THF})_3$ in 10 mL THF was stirred at reflux for 5 hours. The obtained green solid was filtered, washed with THF (3 x 10 mL) and dried under reduced pressure. Yield 0.71 g (91.8%).
- Microanalysis, %: Calc. for $\text{C}_{17}\text{H}_{17}\text{N}_5\text{CrCl}_3$: C 45.38, H 3.78, N 15.57. Found C 45.49, H 3.71, N 15.33. +FAB MS (m/z): $\text{M}-\text{Cl}$: 413. $\mu_{\text{eff.}} = 3.73$ BM. (THF is tetrahydrofuran;
- 10 +FAB MS is Positive Fast Atom Bombardment Mass Spectroscopy; $\mu_{\text{eff.}}$ is magnetic moment.

Examples 3-11 (Table 1)

Ethylene oligomerization/polymerisation tests with Cr-1

- 15 The ethylene oligomerisation/polymerisation tests were carried out using the following procedure.

Preparation of solution of activated catalyst. The required amount of catalyst precursor Cr-1 (0.5 – 5 mg) was suspended in 20 – 100 ml toluene followed by the addition of the co-catalyst (methylalumoxane - MAO, 0.01 – 8 mmol). Thus prepared solution can be used immediately or stored at 0°C for a number of days.

- 20 Ethylene oligomerisation / polymerisation.

- The ethylene oligomerisation/polymerisation reactions were usually carried out in a 400 ml "Fischer-Porter" glass reactor equipped with a gas inlet, a catalyst inlet, a mechanical stirrer and a digital thermometer. An aliquot of 1-5 ml of the catalyst solution described above was added to the reactor containing 200 – 300 ml solvent (usually toluene) and
- 25 0.1 – 5 mmol scavenger (usually triisobutyl aluminium – TIBAL or MAO). The reactor was then connected to the ethylene gas supply at the desired pressure and the

temperature brought to the required value. The reaction was carried out for 10 – 120 min (usually 60 min). The reaction mixture was then quickly cooled down to room temperature (if necessary) and the reaction terminated by venting the ethylene off. GC (Gas Chromatography) samples were always withdrawn and analysed in order to

5 determine the molecular-weight distribution of the C4-C40 olefins: The reactor content was then poured into a beaker containing 400 ml methanol and a few drops of 2M HCL. The precipitated polymer was filtered, washed with methanol and dried at 60°C under vacuum.

Table Cr-10. Polymerisation in toluene

Ex	Cat., μmol	MAO, mmol (#1)	Temp. Set- point, °C (#2)	P C ₂ H ₄ bar	Pol. time, min	ΔT, °C. (Note3)	Soluble fraction g (#4)	Insol. fraction g (#5)	Activity, g/mmol.h. bar (#6)
3	2.70	7.3	20	4	40	+96	8.4	43.7	7240
4	0.50	2.8	20	4	60	+90	15.9	68.1	42050
5	0.18	7.2	20	4	60	+62	9.1	28.7	52500
6	0.07	3.5	20	4	80	+35	8.2	17.5	68840
7	0.03	6.6	50	4	60	+4	2.8	10.3	109170
8	0.03	3.7	50	3	60	+3	2.4	7.9	114400
9	0.03	3.7	50	2	60	+1	1.8	5.9	128300
10	0.03	3.7	50	1	60	0-+1	0.6	2.5	116700
11	0.12	4.3	50	4	60	+8	11.6	22.4	70830

Notes

#1. MAO is methylalumoxane (co-catalyst)

#2. Temperature set-point is the temperature at the start of the polymerisation reaction.

The temperature in the reactor is uncontrolled and will change from this point due to the heat formation during the polymerisation reaction.

#3. ΔT is the difference between the temperature in the reactor and the temperature in the cooling bath

#4. This is the fraction of ethylene oligomers, soluble in toluene at room temperature.

#5. The fraction of ethylene oligomers insoluble in toluene at room temperature

#6. The activity is based on the sum of the soluble and insoluble fractions.

Example 11. In presence of 10 ml 1-hexene.

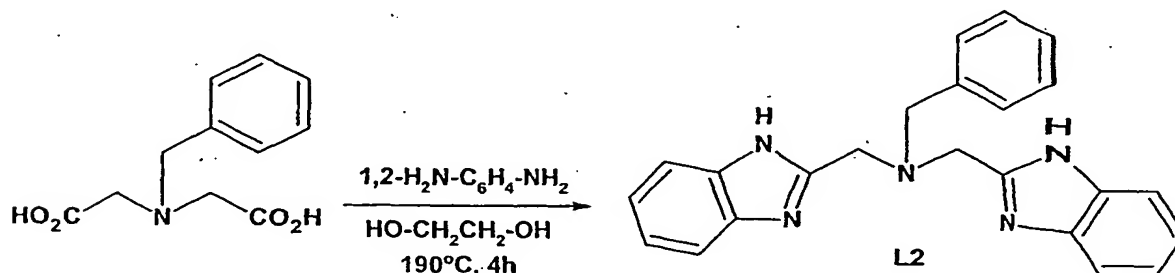
Gas Chromatography traces for the soluble fractions from Examples 3, 7, 8, 9 and 11 are shown in Figures 1, 2, 3, 4 and 5 of the drawings.

The molecular weight distributions of the soluble fractions obtained by CrI can be described by a combination of two distribution curves – a Schulz-Flory type curve for the C_n homologues and an intermediate (Schulz-Flory – Poisson) type curve for the C_{n+2} homologues.

The insoluble fraction consists of low molecular weight polyethylene. For example the insoluble fraction (polyethylene) described in Example 7 has $M_n = 1298$, $M_w = 3537$ and $PDI = 2.62$.

Example 12

Preparation of N,N-bis(1H-benzimidazol-2-ylmethyl)-N-benzylmine (L-2)



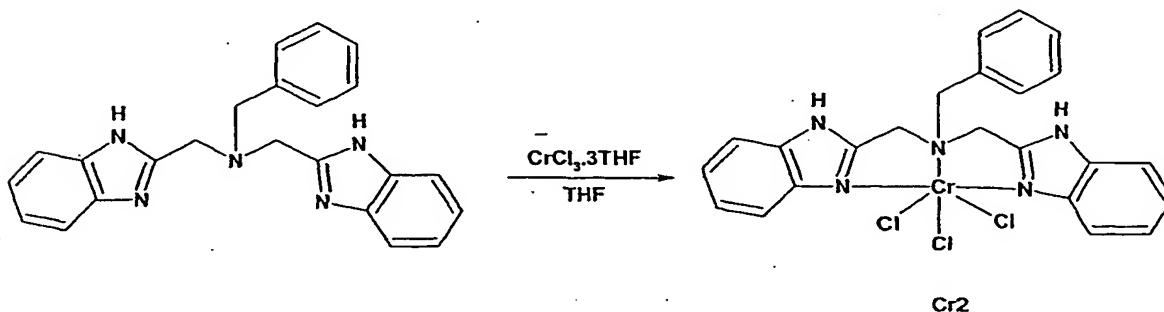
A mixture of 4.00 g (17.9 mmol) N-benzyliminodiacetic acid and 3.86 g (35.8 mmol) o-phenylene diamine in 30 ml ethylene glycol was stirred at 190°C for 4 hours. The

water produced during was distilled off continuously. At the end of the reaction, the reaction mixture was allowed to cool down to room temperature and then poured in 150 ml water. The obtained slurry was triturated for 30 min, filtered, washed with water (3 x 30 ml) and dried at 60°C under reduced pressure for 48 hours. Yield 4.94 g (75.0%). ¹H NMR (250 MHz, DMSO-d₆), δ 3.72 (s, 2H), 3.92 (s, 4H), 7.13-7.57 (m, 13H), 12.37 (Br. s; 2H). +CI MS (m/z): [368]. (+CI-MS is Positive Chemical Ionisation Mass Spectroscopy).

Example 13

Preparation of [N,N-bis(1H-benzimidazol-2-ylmethyl)-N-

10 benzylamine]trichlorochromium(III) (Cr-2)



A slurry of 1.00 g (2.82 mmol) L2 and 1.06 g (2.82 mmol) CrCl₃(THF)₃ in 30 mL THF was stirred at reflux for 4 hours. The obtained green solid was filtered, washed with THF (3 x 15 mL) and dried under reduced pressure. Yield 1.20 g (82.9%).

15 Microanalysis, %: Calc. for C₂₃H₂₁N₅CrCl₃: C 52.54, H 4.03, N 13.32. Found C 52.38, H 3.97, N 13.12. $\mu_{\text{eff.}} = 3.63$ BM. (THF is tetrahydrofuran; $\mu_{\text{eff.}}$ is magnetic moment).

Example 14

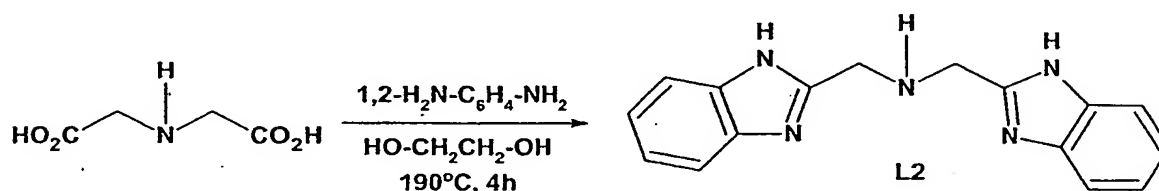
Ethylene oligomerisation/polymerisation test with catalyst Cr-2. Results are given in the Table.

Ex	Cat., μmol	MAO, mmol	Temp. Set-point, °C	P C ₂ H ₄ bar	Pol. time, min	ΔT, °C	Soluble fraction g	Insoluble fraction g	Activity, g/mmol. h.bar
14	10.0	10.0	26	4	60	+60	6.1	42.0	1200

The GC trace for the soluble fraction from Example 14 is shown in Figure 6 of the Drawings.

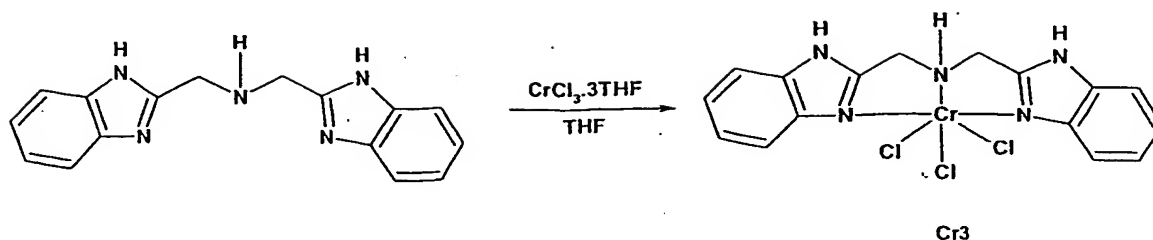
5 Example 15

Preparation of *N,N*-bis(1*H*-benzimidazol-2-ylmethyl)amine (L-3)



A mixture of 3.62 g (27.2 mmol) *N*-iminodiacetic acid and 4.40 g (54.4 mmol) *o*-phenylene diamine in 30 ml ethylene glycol was stirred at 190°C for 4 hours. The water produced during was distilled off continuously. At the end of the reaction, the reaction mixture was allowed to cool down to room temperature and then poured in 150 ml water. The obtained slurry was triturated for 30 min, filtered, washed with water (3 x 30 ml) and dried at 60°C under reduced pressure for 48 hours. Yield 5.28 g (70.0%). ¹H NMR (250 MHz, DMSO-*d*₆), δ 3.40 (br.s, 1H), 4.00 (s, 4H), 7.14 (m, 4H), 7.51 (m, 4H), 12.41 (br. s, 2H).

Preparation of [*N,N*-bis(1*H*-benzimidazol-2-ylmethyl)amine]trichlorochromium(III) (Cr-3)



A slurry of 0.50 g (1.81 mmol) L3 and 0.68 g (1.81 mmol) $\text{CrCl}_3(\text{THF})_3$ in 10 mL THF was stirred at reflux for 4 hours. The obtained green solid was filtered, washed with THF (3 x 15 mL) and dried under reduced pressure. Yield 0.62 g (79.1%).

5 Example 16

Ethylene oligomerisation/polymerisation test with Cr-3

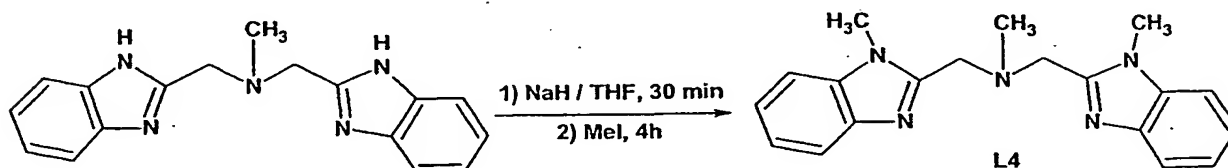
Ex	Cat., μmol	MAO, mmol	Temp. Set-point, $^{\circ}\text{C}$	P C_2H_4 bar	Pol. time, min	ΔT , deg.	Soluble fraction g	Insoluble fraction g	Activity, $\text{g}/\text{mmol.h.}$ bar
16	10.0	10.0	22	4	30	+62	14.4	26.0	2020

The GC trace for the soluble fraction from Example 16 is shown in Figure 7 of the Drawings.

10 Insoluble fraction: $M_n = 807$, $M_w = 1316$, $\text{PDI} = 1.63$.

Example 17

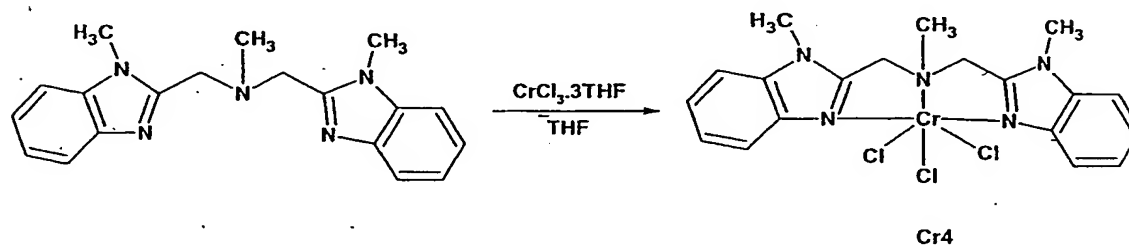
Preparation of N-methyl-N,N-bis[(1-methyl-1H-benzimidazol-2-yl)methyl]amine (L-4)



A mixture of 1.00 g (3.4 mmol) *N,N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine, 0.33 g (13.8 mmol) NaH and 30 ml THF were stirred at room temperature for 30 min. MeI (0.43 ml, 6.8 mmol) was then added and the reaction mixture stirred for another 4 hours. Addition of 120 ml water resulted in the formation of a off-white precipitate which was filtered, washed extensively with water and dried at 60°C under vacuum. Yield 0.81 g (74.0%). ¹H NMR (250 MHz, CDCl₃), δ 2.39 (s, 3H), 3.67 (s, 6H), 3.93 (s, 4H) 7.24 (m, 6H), 7.67 (m, 2H).

Example 18

- 10 Preparation of {*N*-methyl-*N,N*-bis[(1-methyl-1*H*-benzimidazol-2-yl)methyl]amine} trichloro-chromium(III) (Cr-4)



- 15 A slurry of 0.50 g (1.56 mmol) L3 and 0.59 g (1.56 mmol) CrCl₃(THF)₃ in 20 ml THF was stirred at reflux for 4 hours. The obtained green solid was filtered, washed with THF (3 x 10 mL) and dried under reduced pressure. Yield 0.64 g (85.8%).
- Microanalysis, %: Calc. for C₁₈H₁₉N₅CrCl₃: C 47.77, H 4.43, N 14.66. Found C 47.59, H 4.40, N 14.64.

Example 19

- 20 Ethylene oligomerisation/polymerisation test with Cr-4

Ex	Cat., μmol	MAO, mmol	Temp. Set- point, °C	P C ₂ H ₄ bar	Pol. time, min	ΔT deg.	Soluble fraction g	Insoluble fraction g	Activity, g/mmol. h.bar
19	19.0	10.0	28	4	60	+30	12.0	12.5	322

The GC trace for the soluble fraction from Example 19 is shown in Figure 8 of the Drawings.

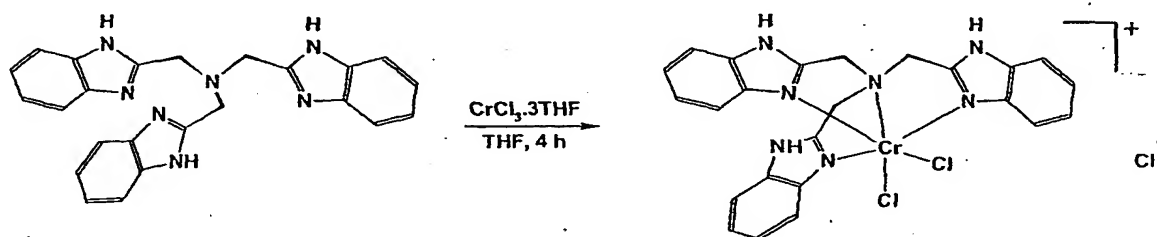
Insoluble fraction: $M_n = 684$, $M_w = 999$, $PDI = 1.46$.

Example 20

5 N,N,N -tris(*1H*-benzimidazol-2-ylmethyl)amine (L5)

Prepared as described in L. K. Thompson et al, Can J. Chem., 55 (1977), 878. 1H NMR (250 MHz, $DMSO-d_6$), δ 4.01 (s, 6H), 7.12 (m, 6H), 7.49 (m, 6H) 12.44 (br. s, 3H).

10 Preparation of {[N,N,N -tris(*1H*-benzimidazol-2-ylmethyl)amine]dichlorochromium (III)} chloride (Cr-5)



Prepared as described in A. E. Cenciers-Gomes, Polyhedron, 19 (2000), 1821. +FAB MS (m/z): 531.

15 Ethylene oligomerisation/polymerisation test with Cr-5. The conditions are shown in the Table.

Ex	Cat., μmol	MAO, mmol	Temp. Set- point, $^{\circ}\text{C}$	P C_2H_4 bar	Pol. time, min	ΔT , deg.	Soluble fraction g	Insoluble fraction g	Activity, g/mmol.h. bar
19	20.0	10.0	20	4	70	+16	4.5	12.5	182

The GC trace for the soluble fraction from Example 20 is shown in Figure 9.

Insoluble fraction: $M_n = 800$, $M_w = 1200$, $PDI = 1.50$

Examples 21-23

Ethylene oligomerisation/polymerisation test with Cr-5.

The conditions are shown in the following Table.

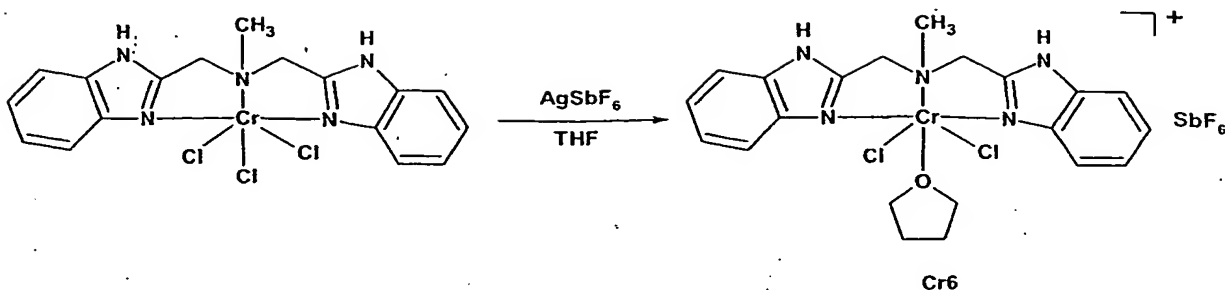
Ex	Cat., μmol	Co-Cat., (mmol) (Note1)	Temp Set- point, °C	P C ₂ H ₄ Bar	Pol. time, min	ΔT, deg.	Soluble fraction g	Insoluble fraction g	Activity, g/mmol. h.bar
21	20.0	PMAO (10)	20	4	60	+2	1.0	3.0	50
22	20.0	MMAO (10)	20	4	60	+2	1.2	3	52
23	20.0	MAO (10)	20	1	60	+1	0.7	1.5	36

- 5 Note 1. PMAO (polymethylalumoxane) is obtained by removing the present trimethylaluminum in the commercial methylalumoxane by distillation under reduced pressure followed by washing with n-heptane. MMAO (modified methylalumoxane) contains triisobutylaluminium and is commercially supplied as solution in hexanes. Example 23. In presence of ethylene (1 bar) and propylene (2 bar).

- 10 GC curves for the soluble fractions in Example 21 are shown in Figure 10; for Example 22 in Figure 11 and for Example 23 in Figure 12.

Example 24

[*N,N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine]dichlorotetrahydrofurano-chromium (III) hexafluoroantimonate (Cr-6).



- A slurry of silver hexafluoroantimonate (0.62 g, 1.82 mmol) [*N,N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine]trichlorochromium(III) (Cr1) (0.50 g, 1.11 mmol) in 50 ml THF was stirred at room temperature for 48 hours. The solution was filtered and the solvent removed under reduced pressure. Yield 0.33 g (53.0 %). +FAB MS (*m/z*): [413]. -FAB MS (*m/z*): [237].

Example 25

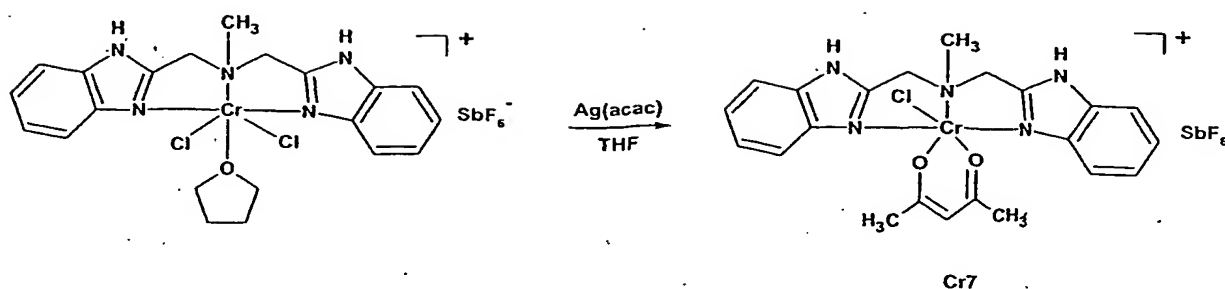
Ethylene oligomerisation/polymerisation test with Cr-6

Ex	Cat., μmol	MAO, mmol	Temp. Setpoint, °C	P C ₂ H ₄ bar	Pol. time, min	ΔT, deg.	Soluble fraction g	Insoluble fraction g	Activity, g/mmol. h.bar
25	0.5	4.2	20	4	60	-	5.8	16.0	10900

10

Example 26

Preparation of [*N,N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine]-2,4-pentanedionatodichloro-chromium (III) hexafluoroantimonate (Cr-7)



Silver acetylacetonate (0.11 g, 0.55 mmol) and [N,N-bis(1H-benzimidazol-2-ylmethyl)-N-methylamine]dichlorotetrahydrofuran-chromium (III) hexafluoroantimonate (Cr6) (0.40 g, 0.55 mmol) were dissolved in THF and stirred at room temperature for 48 hours. After filtering, the solvent was removed, the residues re-dissolved in dichloromethane, filtered and layered with pentane to afford suitable crystals for X-ray diffraction. Yield 0.32 g (82.0 %). Microanalysis, %: Calc. for C₂₂H₂₃ClCrF₆N₅O₂Sb: C 37.0, H 3.23, N 9.83. Found C 36.68, H 3.36, N 9.57. +FAB MS (m/z): [477]. -FAB MS (m/z): [235]. (-FAB MS is Negative Fast Atom Bombardment Mass Spectroscopy).

The molecular structure of complex Cr-7 is shown in Figure 13 of the Drawings

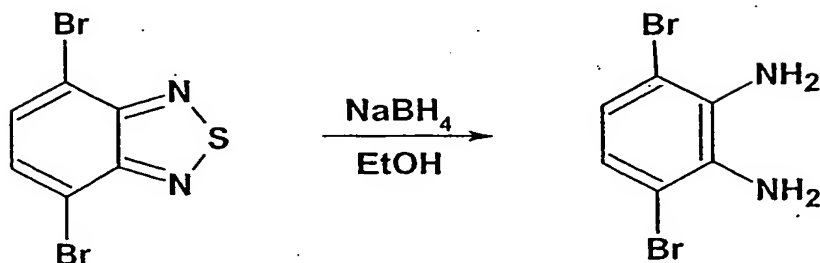
Example 27

Ethylene oligomerisation/polymerisation test with catalyst complex Cr-7

Example	Cat., μmol	MAO, mmol	Temp. Setpoint, °C	P C ₂ H ₄ bar	Pol. time, min	ΔT, deg.	Soluble fraction g	Insoluble fraction g	Activity, g/mmol. h.bar
25	0.5	4.2	20	4	60	-	4.8	22.0	13400

Example 28

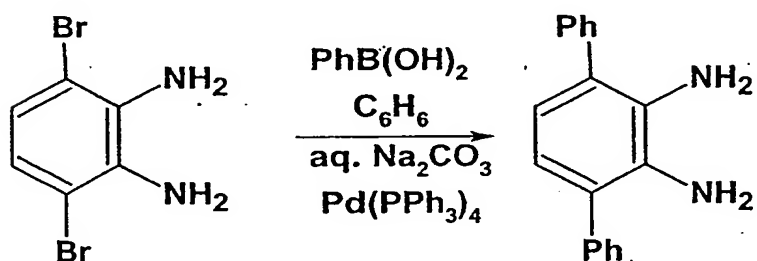
Preparation of 2-Amino-3,6-dibromophenylamine



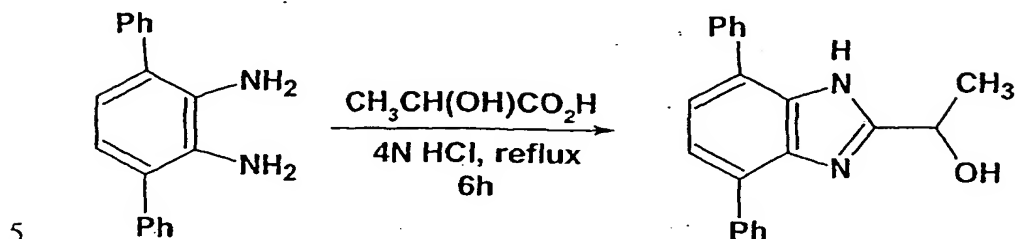
- 5 A mixture of 4,7-dibromo-2,1,3-benzothiadiazole (synthesized according to as described in K. Pilgram, J. Heterocycl. Chem., 7 (1970), 629) (16.0 g, 54.4 mmol) and NaBH₄ (38.1 g, 1.0 mol) in 500 ml ethanol was stirred at room temperature for 30 hours. The solvent was evaporated and the residue mixed with 500 ml water. The obtained mixture was extracted into diethyl ether (5 x 150 ml). The combined extracts were washed with
- 10 brine (2 x 100 ml) and dried over anhydrous Na₂SO₄. Evaporation of the solvent and drying under reduced pressure afforded 11.5 g (79.5 %) of the product.

Example 29

1,1':4',1''-Terphenyl-2',3'-diamine

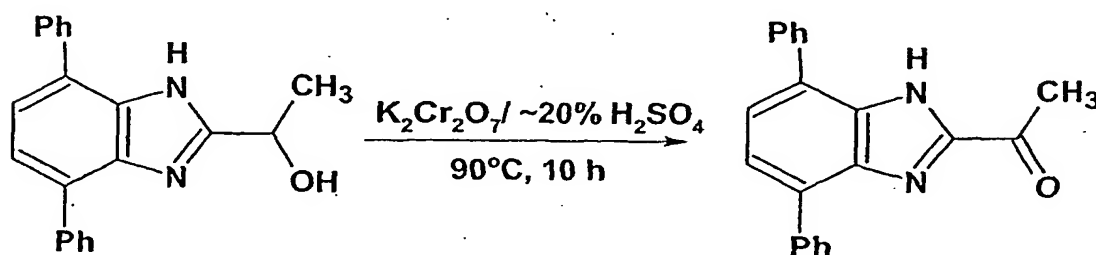


- 15 To a solution of 3.60 g (13.5 mmol) 2-amino-3,6-dibromophenylamine in 135 ml degassed benzene was added a solution 4.95 g (40.6 mmol) phenylboronic acid in 30 ml ethanol, followed by 54 ml 2M aqueous Na₂CO₃ and 1.89 g (1.62 mmol) solid Pd(PPh₃)₄. The dark-blue reaction mixture was refluxed for 24 hours and then allowed to cool down to room temperature. The aqueous layer was decanted and washed twice
- 20 with 20 ml ethyl acetate. The combined organic layers were washed with water (2 x 50 ml), dried over anhydrous Na₂SO₄ and evaporated. The residue was purified by flash chromatography (SiO₂, 20% EtOAc / 80% n-hexane). Yield – 1.6 g (45.4 %). ¹H NMR (250 MHz, CDCl₃), δ, ppm: 3.63 (br. s, 4H), 6.81 (s, 2H), 7.39 (m, 2H), 7.50 (m, 8H).

Example 30Preparation of 1-(4,7-Diphenyl-1*H*-benzimidazol-2-yl)ethanol

A mixture of 1.25 g (4.8 mmol) 1,1':4',1''-terphenyl-2',3'-diamine, 0.75 ml (8.6 mmol) 85% aq. lactic acid and 4.8 ml 4N HCl were stirred at reflux for 6 hours and then the volatile materials evaporated over 1 hour. The oily residue was heated to 140°C and stirred for 15 min. After cooling to room temperature 10 ml water were added and the mixture triturated for 30 min. Addition of conc. NH_4OH to pH~7.5-8 followed by filtration, washing with water (4 x 10 ml) and drying under vacuum at 60°C gave 1.25g (82.8 %) of the desired product. ^1H NMR (250 MHz, CDCl_3), δ , ppm: 1.58 (d, $J_{\text{HH}} = 6.7$ Hz, 3H), 3.64 (br.s, 1H), 5.07 (q, 1H), 7.37-7.76 (m, 12 H), 9.53 (br. s, 1H).

10

Example 3115 Preparation of 1-(4,7-Diphenyl-1*H*-benzimidazol-2-yl)ethanone

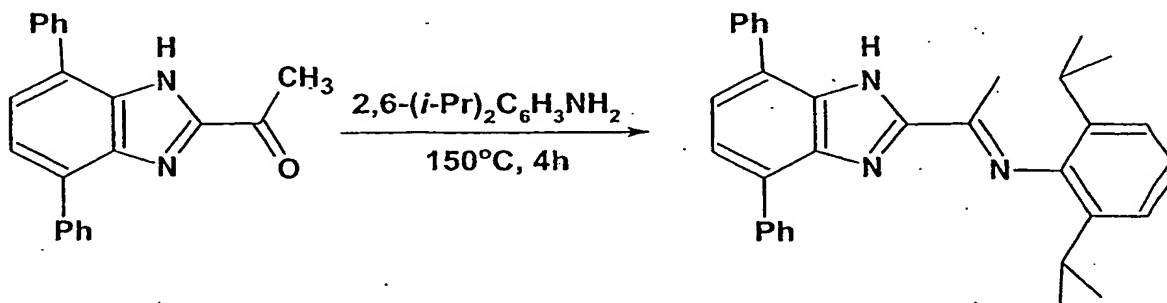
A solution of 1.38g (4.7 mmol) potassium dichromate in 8.5 ml 40% H_2SO_4 was added dropwise to a stirred suspension of 1.10g (3.5 mmol) 1-(4,7-diphenyl-1*H*-benzimidazol-2-yl)ethanol in 15 ml 5% H_2SO_4 . The slurry was stirred at 90°C for 10 hours, cooled to room temperature and treated with 7 ml conc. NH_4OH . The residue was filtered, washed with water (5 x 10 ml) and extracted with acetone (10 x 30 ml). The combined extracts were filtered through a 0.5 cm layer of silica and the filtrate evaporated. The residue was

20

re-crystallized from ethyl acetate-cyclohexane. Yield – 0.57g (52.1%). ¹H NMR (250 MHz, CDCl₃), δ, ppm: 2.83 (s, 3H), 7.44-7.64 (m, 10H), 8.14 (d, 7.6 Hz, 2H), 10.22 (br.s).

5 Example 32

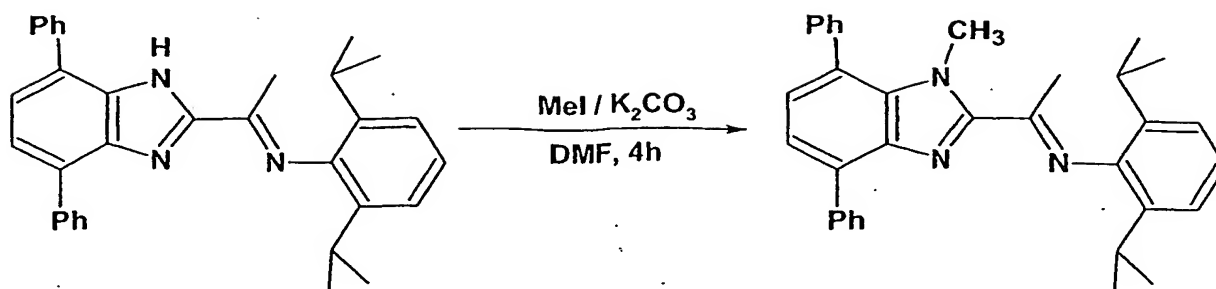
Preparation of N-[(1E)-1-(4,7-diphenyl-1H-benzimidazol-2-yl)ethylidene]-N-(2,6-diisopropylphenyl)-amine



A mixture of 0.25g (0.8 mmol) 1-(4,7-diphenyl-1H-benzimidazol-2-yl)ethanone, 0.6 ml diisopropyl aniline and a drop of glacial acetic acid was stirred at 150°C for 4 hours. The unreacted aniline was removed at 150°C under reduced pressure, the residual oil cooled to room temperature and triturated with 5 ml pentane at room temperature for 20 min. The mixture was then cooled to –20°C, triturated for another 5 min. and filtered while cold. The solid was washed with cold (–5°C) pentane (2 x 2 ml) and dried under reduced pressure. Yield – 0.28 g (74.2%). Microanalysis, %: Calc. for C₃₃H₃₃N₃: C 84.08, H 7.26, N 8.65. Found C 84.10, H 7.14, N 8.71. ¹H NMR (250 MHz, CDCl₃), δ, ppm: 1.15 (dd, J_{HH} = 3.1 Hz, J_{HH} = 7.1 Hz, 12 H), 2.36 (s, 3H), 2.76 (m, 2H), 7.17 (m, 3H), 7.53 (m, 8H), 7.72 (dd, J_{HH} = 1.5 Hz, J_{HH} = 6.9 Hz, 2H), 8.20 (dd, J_{HH} = 1.2 Hz, J_{HH} = 7.0 Hz, 2H), 10.42 (br.s 1H).

20 Example 33

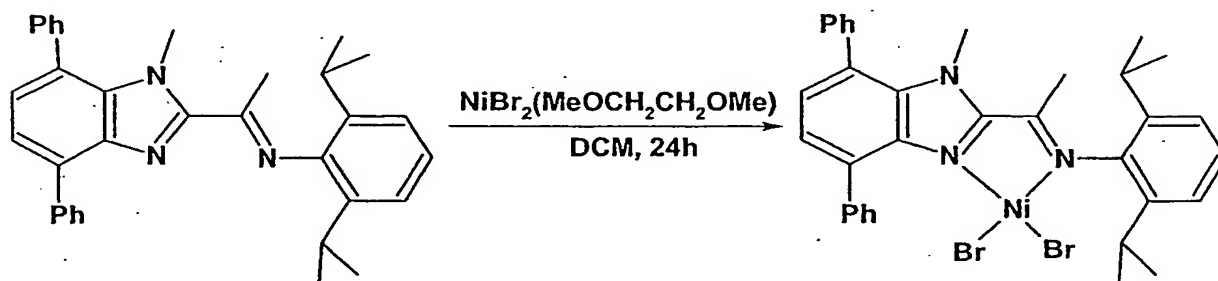
Preparation of N-(2,6-diisopropylphenyl)-N-[(1E)-1-(1-methyl-4,7-diphenyl-1H-benzimidazol-2-yl)ethylidene]amine (L-6)



A mixture of 0.25 g (0.53 mmol) *N*-[(1*E*)-1-(4,7-diphenyl-1*H*-benzimidazol-2-yl)ethylidene]-*N*-(2,6-diisopropylphenyl)-amine, 0.41 g (3.0 mmol) anhydrous K_2CO_3 and 0.08 g (0.56 mmol) MeI in 4 ml anhydrous DMF was stirred at room temperature for 10 hours. The reaction mixture was then poured into 50 ml water, stirred for 10 min and extracted with ethyl acetate (3 x 30 ml). The combined extracts were washed with water (3 x 15 ml) and dried over anhydrous Na_2SO_4 . The solvent was evaporated to give a yellow oil which was triturated with 5 ml methanol at $-78^\circ C$, filtered while cold, washed with cold ($-78^\circ C$) methanol (2 x 2 ml) and dried under reduced pressure. Yield 0.16 g (62.2 %). 1H NMR (250 MHz, $CDCl_3$), δ , ppm: 1.14 (dd, $J_{HH} = 7.0$ Hz, $J_{HH} = 15.0$ Hz, 12 H), 2.38 (s, 3H), 2.75 (m, 2H), 3.87 (s, 3H) 7.14 (m, 3H), 7.29 (d, 7.6 Hz, 1H), 7.53 (m, 9H), 7.72 (dd, $J_{HH} = 1.5$ Hz, $J_{HH} = 6.9$ Hz, 2H), 8.19 (dd, $J_{HH} = 1.2$ Hz, $J_{HH} = 7.1$ Hz, 2H).

Example 34

Preparation of {*N*-(2,6-diisopropylphenyl)-*N*-[(1*E*)-1-(1-methyl-4,7-diphenyl-1*H*-benzimidazol-2-yl)ethylidene]amine} dibromonickel (II). (Ni-1)



A slurry of 0.07g (0.14 mmol) *N*-(2,6-diisopropylphenyl)-*N*-[(1*E*)-1-(1-methyl-4,7-diphenyl-1*H*-benzimidazol-2-yl)ethylidene]amine and nickel dibromide dimethoxy ethane complex (0.04 g (0.14 mmol) in 5 ml dichloromethane (DCM) was stirred at

room temperature for 24 hours. The solid was filtered, washed with DCM (3 x 5 ml) and dried under reduced pressure. Yield 0.09 g (88.7 %). The crystal structure of Ni1 is shown in Figure 14.

Example 35

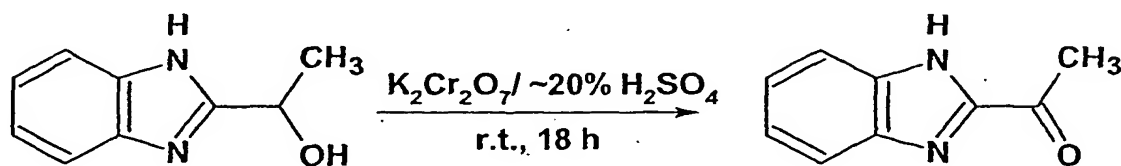
5 Ethylene polymerisation test with Ni-1

Ex	Cat., μmol	MAO, mmol	Temp. Setpoint, °C	P C ₂ H ₄ bar	Pol. time, min	ΔT, deg.	Soluble fraction g	Insoluble fraction g	Activity, g/mmol. h.bar
25	9.9	1	22	1	30	-	-	0.2	40

Example 36

Preparation of 1-(1*H*-benzimidazol-2-yl)ethanone

As described in J. Kollonisch, US Pat. 3,320 273 /16.5.1967.



10

A solution of 16.2 g (0.1 mol) 1-(1*H*-benzimidazol-2-yl)ethanol (synthesised according to as described in A. Katrizky et al. Tetrahedron Asymmetry, 8 (1997), 1491) in 200 ml 5% H₂SO₄ was treated with a solution of 39.6g (75.5 mmol) potassium dichromate in 40% sulphuric acid. The reaction mixture was stirred at room temperature for 18 hours and neutralised with 190 ml conc. NH₄OH. The formed precipitate was filtered, washed with 700 ml water and extracted with 700 ml 96% ethanol. The solvent was evaporated to c.a. 50-80 ml, the formed suspension cooled to -40°C, stirred for 10 min and filtered while cold. The solid was washed with 2x 10 ml cold ethanol and dried under reduced pressure. Yield - 9.3 g (58.1 %). ¹H NMR (250 MHz, CDCl₃), δ, ppm: 2.84 (s, 3H), 7.38 (m, 2H), 7.56 (d, J_{HH} = 7.3 Hz, 1H), 7.89 (d, J_{HH} = 7.6 Hz, 1H), 11.08 (br.s 1H).

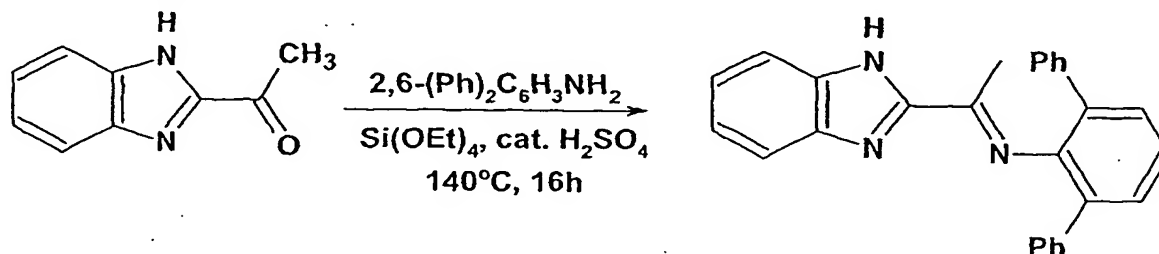
15

20

Example 37

Preparation of *N*-[(1*E*)-1-(1*H*-benzimidazol-2-yl)ethylidene]-*N*-1,1':3',1''-terphenyl-2'-ylamine

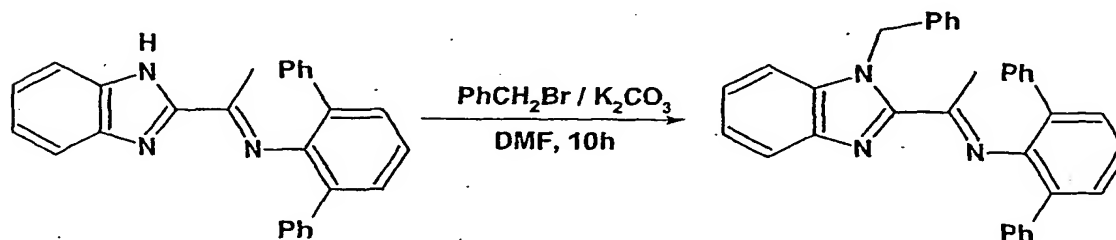
Similarly to the method described in M. Ali et. al., Z Naturforsch. B. Anorg. Chem. Org. Chem., 31 (1976), 254



A mixture of 0.8 g (3.26 mmol) 1-(1*H*-benzimidazol-2-yl)ethanone, 0.52g (3.26 mmol) 2,6-diphenylaniline, 0.45g (3.75 mmol) tetraethylorthosilicate [(EtO)₄Si] and 1 drop conc. sulfuric acid was stirred at 140°C for 16 hours. The volatile materials were evaporated, the residue cooled to room temperature and 5-6 ml methanol were added. The precipitate was filtered, washed with 5 ml cold methanol and extracted into 20 ml dichloromethane. The extract was filtered and the filtrate evaporated to give 1.2 g (76.3 %) of the desired product. Microanalysis, %: Calc. for C₂₇H₂₁N₃: C 83.69, H 5.46, N 10.84. Found C 83.79, H 5.52, N 10.68. ¹H NMR (250 MHz, CDCl₃), δ, ppm: 1.97 (s, 3H), 2.74 (m, 2H), 7.22 (m, 8H), 7.36 (m, 8H), 7.75 (J_{HH} = 7.3 Hz, 1H), 10.0 (br.s, 1H).

Example 38

Preparation of *N*-[(1*E*)-1-(1-benzyl-1*H*-benzimidazol-2-yl)ethylidene]-*N*-1,1':3',1''-terphenyl-2'-ylamine (L-7)

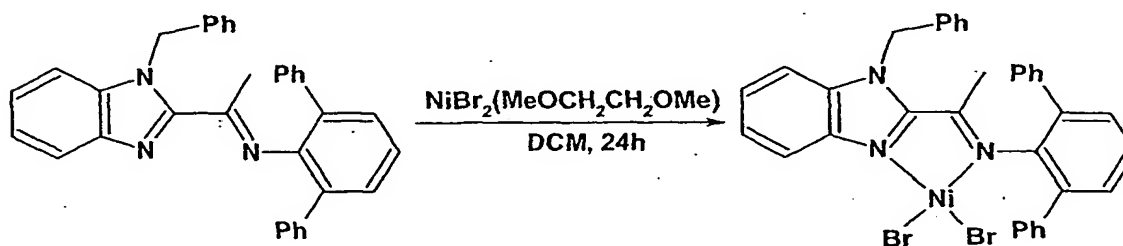


A mixture of 0.70 g (1.87 mmol) *N*-[(1*E*)-1-(1*H*-benzimidazol-2-yl)ethylidene]-*N*-1,1':3',1''-terphenyl-2'-ylamine, 1.42 g (10.3 mmol) anhydrous K₂CO₃ and 0.35 g (2.06 mmol) benzylbromide in 4 ml anhydrous DMF was stirred at room temperature for 10

hours. The reaction mixture was then poured into 80 ml water, stirred for 10 min and extracted with ethyl acetate (3 x 50 ml). The combined extracts were washed with water (3 x 25 ml) and dried over anhydrous Na_2SO_4 . The solvent was evaporated to give an yellow oil which was triturated with 5 ml methanol at -78°C , filtered while cold, washed with cold (-78°C) methanol (2 x 2 ml) and dried under reduced pressure. Yield 0.56 g (66.2 %). ^1H NMR (250 MHz, CDCl_3), δ , ppm: 2.07 (s, 3H), 5.51 (m, 2H), 6.90 (m, 2H) 7.22 (m, 19H), 7.78 (m, 1H).

Example 39

Preparation of {*N*-[(1*E*)-1-(1-benzyl-1*H*-benzimidazol-2-yl)ethylidene]-*N*-1,1':3',1''-terphenyl-2'-ylamine}dibromonickel (II) (Ni-2)



A slurry of 0.30 g (0.65 mmol) *N*-[(1*E*)-1-(1-benzyl-1*H*-benzimidazol-2-yl)ethylidene]-*N*-1,1':3',1''-terphenyl-2'-ylamine and nickel dibromide dimethoxy ethane complex (0.19 g, 0.65 mmol) in 20 ml dichloromethane (DCM) was stirred at room temperature for 24 hours. The solid was filtered, washed with DCM (3 x 10 ml) and dried under reduced pressure. Yield 0.40 g (90.2 %).

Examples 40-42

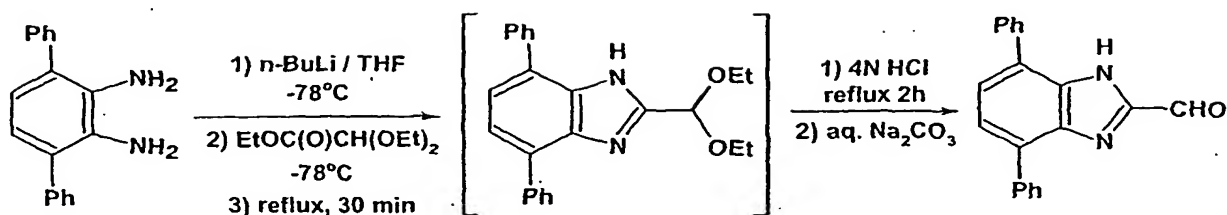
Ethylene oligomerisation tests with Ni-2 – See Table below

Ex	Cat., μmol	MAO, mmol	Temp. Setpoint, °C	P C ₂ H ₄ bar	Pol. time, min	ΔT, deg.	Soluble fraction g	Insoluble fraction g	Activity, g/mmol. h.bar
40	10.0	1.0	23	4	60	+19	11.9	-	298
41	10.0	1.0	24	5	60	+23	15.2	-	304
42	10.0	1.0	23	2	60	+11	6.0	-	300

5 Examples 40-42 - Oligomer analysis

Exam ple	Mn	Mw	PDI	Linear olefins, mol %	Internal olefins, mol%
40	370	590	1.60	94.6	87.5
41	370	640	1.64	94.7	83.8
42	390	630	1.64	94.6	83.8

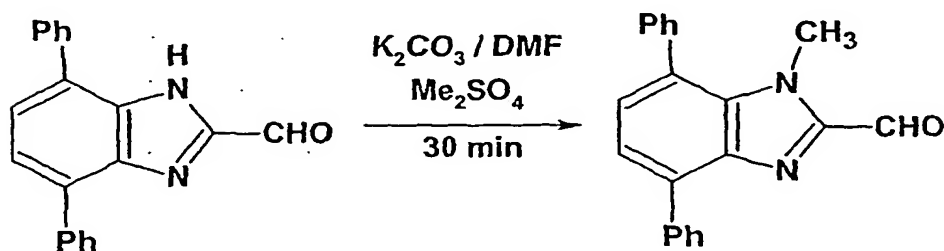
Example 43Preparation of 4,7-Diphenyl-1*H*-benzimidazole-2-carbaldehyde



A solution of 11.1 ml (27.72 mmol) n-BuLi (2.5 M in hexanes) was added dropwise to a cooled to -78°C solution of 3.4 g (13.2 mmol) 1,1':4,1''-terphenyl-2',3'-diamine in 110 ml THF. The reaction mixture was stirred at -78°C for 1 hour and 2.4 ml (13.5 mmol) dry ethyl diethoxyacetate were added dropwise over 1 min. The solution was then stirred at 78°C for 30 min, allowed to slowly warm up room temperature, stirred for another 30 min and the heated at reflux for 2 hours. Formation of white precipitate (LiOH) was observed during the reflux. After cooling to room temperature and addition of 60 ml water the reaction mixture was carefully neutralized with the addition of 5N acetic acid. Diethyl ether (200 ml) was then added, the formed biphasic mixture was vigorously stirred and the organic layer separated. It was washed with water (3 x 100 ml) and dried over anhydrous sodium sulfate. Evaporation of the solvent afforded an yellow-brown oil which was dissolved in 15 ml THF and 60 ml 4N HCl were added. The mixture was stirred at reflux for 2 hours, cooled to room temperature and 120 ml icy water was added. The mixture was stirred vigorously for 10 min at $\sim 0^{\circ}\text{C}$ and then filtered. The solid was suspended in 70 ml water and neutralized with 10% aqueous sodium carbonate. The solid was filtered again, washed with water and dried at room temperature under reduced pressure. Yield – 2.85 g (72.4%). ^1H NMR (250 MHz, CDCl_3), δ , ppm: 7.54 (m, 10H), 8.03 (br. s, 2H), 10.06 (s, 1H), 10.31 (br. s, 1H).

Example 44

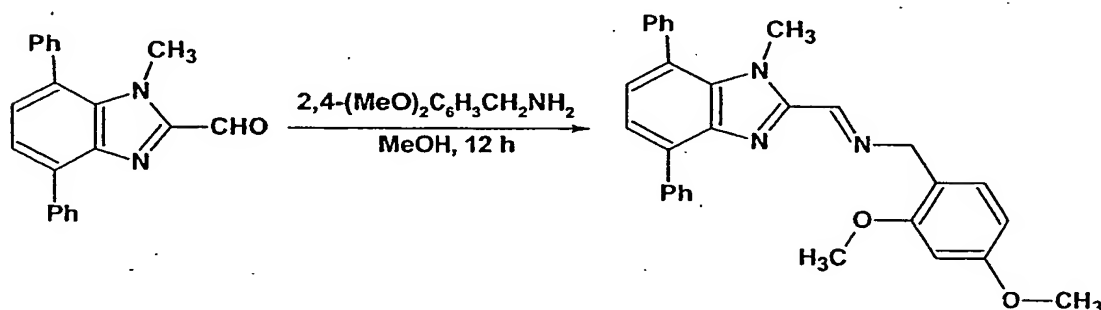
Preparation of 1-Methyl-4,7-diphenyl-1H-benzimidazole-2-carbaldehyde



A mixture of 3.3 g (11.07 mmol) 4,7-diphenyl-1*H*-benzimidazole-2-carbaldehyde, 8.60 g (62.0 mmol) anhydrous K₂CO₃ and 1.1 ml (11.07 mmol) dimethyl sulfate in 30 ml anhydrous DMF was stirred at room temperature for 30 min. The reaction mixture was then poured into 300 ml water, stirred for 10 min and extracted with dichloromethane (3 x 100 ml). The combined extracts were washed with water (3 x 50 ml) and dried over anhydrous Na₂SO₄. The solvent was evaporated to give an yellow oil which was triturated with 20 ml methanol at 0°C, filtered while cold, washed with cold (0°C) methanol (2 x 10 ml) and dried under reduced pressure. Yield 3.1 g (89.6 %). ¹H NMR (250 MHz, CDCl₃), δ, ppm: 3.74 (s, 3H), 7.47 (m, 10H) 8.04 (d, J_{HH} = 7.8 Hz, 2H), 10.1 (s, 1H).

Example 45

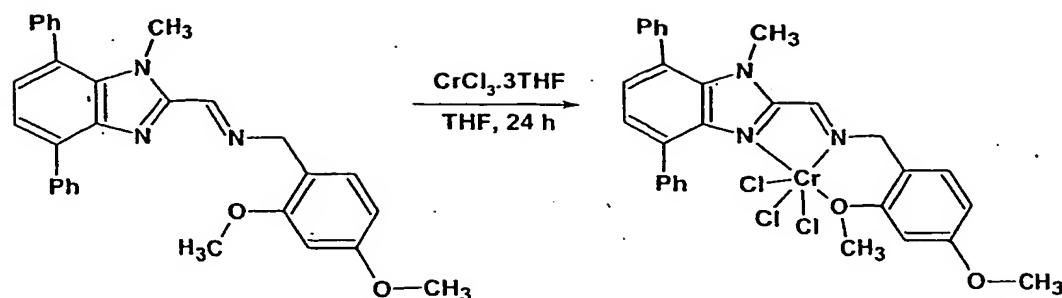
Preparation of *N*-(2,4-dimethoxybenzyl)-*N*-[(1*E*)-(1-methyl-4,7-diphenyl-1*H*-benzimidazol-2-yl)methylene]amine (L8)



A mixture of 0.1 g (0.32 mmol) 1-methyl-4,7-diphenyl-1*H*-benzimidazole-2-carbaldehyde, 55 mg (0.32 mmol) 2,4-dimethoxybenzylamine and 1 drop glacial acetic acid in 8 ml methanol were stirred for 12 hour at room temperature. The reaction mixture was cooled to -20°C and filtered while cold. The solid was washed with cold (-20°C) methanol (2 x 1 ml) and dried at reduced pressure. Yield - 0.12g (81.1%). ¹H NMR (250 MHz, CDCl₃), δ, ppm: 3.76 (s, 3H), 3.80 (s, 6H), 4.81 (s, 2H), 6.46 (m, 2H), 7.14 (d, J_{HH} = 8.8 Hz, 1H), 7.25 (d, J_{HH} = 7.6 Hz, 1H), 7.46 (m, 9H), 8.02 (d, J_{HH} = 7.0 Hz, 2H), 8.61 (s, 1H).

Example 46

Preparation of {*N*-(2,4-dimethoxybenzyl)-*N*-[(1*E*)-(1-methyl-4,7-diphenyl-1*H*-benzimidazol-2-yl)methylene]amine} trichlorochromium (III) (Cr-8).



- 5 A solution of 47 mg (0.1 mmol) *N*-(2,4-dimethoxybenzyl)-*N*-[(1*E*)-(1-methyl-4,7-diphenyl-1*H*-benzimidazol-2-yl)methylene]amine and 36 mg (0.1 mmol) tris(tetrahydrofuran)chromium trichloride in 5 ml THF was stirred at room temperature for 24 hours. The volume of the reaction mixture was reduced to c.a. 1 ml and 10 ml *n*-pentane were added. The formed precipitate was filtered, washed with pentane (2 x 2 ml) and dried
- 10 under reduced pressure. Yield – 44 mg (72.0 %).

Example 47

Ethylene polymerisation test with Cr-8

Ex	Cat., μmol	MAO, mmol	Temp. Setpoint, °C	P C ₂ H ₄ bar	Pol. time, min	ΔT, deg.	Polymer Yield, g	Activity, g/mmol. h.bar
47	10.0	7.0	20	1	50	-	3.5	420

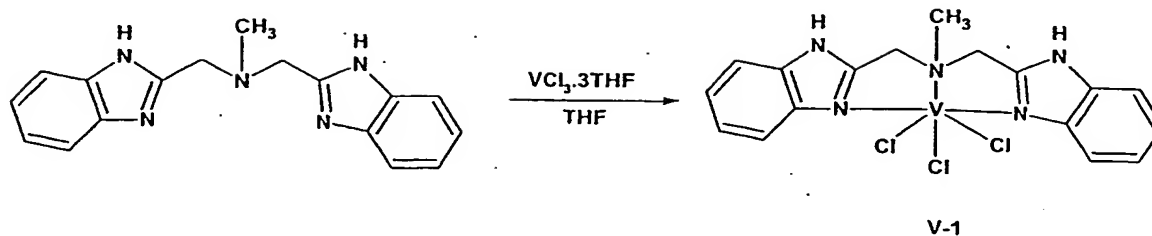
Example 47 – polymer properties

Ex.	Mn	Mw	PDI
47	1421	52600	37.0

15

Example 48

Preparation of [*N,N*-bis(1*H*-benzimidazol-2-yl)methyl)-*N*-methylamine]trichlorovanadium(III) (V-1)



A slurry of 12.00 g (41.2 mmol) L-1 and 15.4 g (41.2 mmol) $\text{VCl}_3(\text{THF})_3$ in 120 mL THF was stirred at reflux for 30 min. The reaction mixture was then allowed to cool down to room temperature and stirred for another 4 hours. The obtained yellow-green solid was filtered, washed with THF (4 x 70 mL) and dried under reduced pressure. Yield 17.8 g (96.2%). Microanalysis, %: Calc. for $\text{C}_{17}\text{H}_{17}\text{N}_5\text{VCl}_3$: C 45.51, H 3.82, N 15.61. Found C 45.39, H 3.62, N 15.41. FT-IR (KBr): 3244, 1596, 1210, 1049, 1003, 982, 944, 752, 701, 653, 621, 518, 475, 455, 432, 416. $\mu_{\text{eff}} = 2.89 \text{ BM}$.

Examples 48-61

10 Ethylene homopolymerisation with V-1

The ethylene homopolymerisation tests were carried out using a procedure similar to that described in Example 3 -11.

Solution of activated catalyst:

The required amount of catalyst precursor V-1 (0.5 – 5 mg) was suspended in 20 – 100 ml toluene followed by the addition of the co-catalyst (DEAC – diethyl aluminium chloride or DMAC – diethylaluminium chloride - 0.1 – 10 mmol). Thus prepared solution can be used immediately or stored at 0°C for a number of days.

Ethylene polymerisation

The ethylene polymerisation reactions were carried out either in a 400 ml “Fischer-Porter” glass reactor (FPR) equipped with a gas inlet, a catalyst inlet, a mechanical stirrer and a digital thermometer or in a 1L stainless-steel reactor (SSR) equipped with an integral system for control of reaction temperature, ethylene pressure and ethylene flow. An aliquot of 1-5 ml of the catalyst solution described above was injected in the reactor containing 200 – 300 (FPR) or 400- 800 (SSR) ml solvent (usually toluene, n-hexane, n-heptane or isobutane), 0.1 – 2 mmol scavenger (usually DMAC) and 10 –60 μmol reactivator (usually ethyl trichloroacetate – ETA or another chlorinated compound as chloroform). The reactor was then connected to the ethylene gas supply at the desired pressure and the temperature brought quickly to the required value. The reaction was

carried out for 10 – 120 min (usually 60 min). The reaction mixture was then cooled down to room temperature (if necessary) and the reaction terminated by venting the ethylene off. If toluene was used as a polymerisation medium, the reactor content was then poured into a beaker containing 400 ml methanol and a few drops of 2M HCl. The polymer was filtered, washed with methanol (if necessary) and dried at 60°C under vacuum.

Table V-1H. Polymerisation in toluene; Fisher-Porter glass reactor

Table V-1H.									
Ex	Cat., μmol	Me ₂ AlC l mmol Note 1	ECA mmol	C ₂ H ₄ bar	H ₂ L	T °C Note 2	Time min	PE g	Activity g mmol ⁻¹ h ⁻¹ bar ⁻¹
48	2.00	0.5	0.01	4	-	50-60	25	10.0	3000
49	1.00	0.25	0.01	4.0	-	50-62	15	7.1	7100
50	0.1	0.25	0.01	4.7	0.3	52-60	60	13.3	20200
51	0.07	0.50	0.1	4.8	0.2	60-68	60	10.6	31550
52	0.07	0.50	0.1	4.8	0.3	60-65	45	8.4	33300
53	0.45	1.00	0.04	4.6	0.3	25-74	60	19	9180
54	0.45	1.00	0.04	3.7	0.3	25-75	60	17.6	10570
55	0.45	1.00	0.04	2.9	0.3	25-58	60	12.6	9655
56	0.45	1.00	0.04	2.1	0.3	25-51	60	10.0	10580
57	0.45	1.00	0.04	1.1	0.3	25-43	60	5.7	11515
58	0.18	0.7	0.02	4	0.2	30-40	60	13.4	18600
59	0.18	0.70	0.02	4	0.2	40-52	60	15	20833
60	0.18	0.70	0.02	4	0.2	50-62	40	9.6	20000
61	0.20	0.60	0.02	4	0.2	85	60	3.4	4250

Polymer properties

Ex.	Mn	Mw	PDI		Ex.	Mn	Mw	PDI
48	157151	714400	4.55		56	140119	338308	2.41
49	p.s.	p.s.	p.s.		57	127175	595700	2.40
50	142900	379800	2.7		58	153077	624458	2.26
51	165600	411100	2.5		59	100404	494179	2.47
52	120700	297500	2.5		60	74901	381329	2.51
55	134222	338648	2.52		61	34197	167406	2.44

Note 1 Me₂AlCl = dimethylaluminium chloride – DMAC;

Run 51: Et₂AlCl (diethylaluminium chloride – DEAC) used as cocatalyst

Runs 53 – 61: the amount of Me₂AlCl shown includes the amount of the scavenger (0.5 mmol)

Note 2 - ECA = ethyl trichloroacetate - C₂H₅OC(O)CCl₃

Note 3 - Temperature left uncontrolled during the polymerisation reaction. The change is due to the heat formation during the polymerisation reaction.

Examples 62-69

10 Ethylene copolymerisation with V-1

The ethylene copolymerisation tests were carried out using a procedure similar to that described in Example 48 - 61. The required amounts of comonomer were preloaded in the polymerisation reactor.

Table V-1C. Polymerisation in toluene. Fisher-Porter glass reactor.

15

Table V-1C.

Ex	Cat., μmol	Me ₂ Al Cl mmol	ECA mmol Note 1	C ₂ H ₄ bar	Co-M mmol Note 2	H ₂ L	T °C Note 3	Time min	Yield g	Activity g mmol ⁻¹ h ⁻¹ bar ⁻¹
62	1.00	0.25	0.01	4.0	C ₃ H ₆ (90)	-	50	15	5.3	5300
63	0.08	0.2	0.01	3.9	C ₃ H ₆ (57)	0.2	60-62	60	5.2	16670
64	0.18	0.7	0.02	2.0	C ₃ H ₆ (96)	0.5	50	60	3.2	8890
65	0.11	0.05	0.01	4.8	1-H (30)	0.1	60-64	60	6.4	10582
66	0.40	1.6	0.05	5	NB (52)	-	50-75	10	9.0	27000
67	0.40	1.6	0.05	5	NB (104)	-	50-66	20	9.7	11640
68	0.40	1.6	0.05	3	NB (120)	-	50	90	8.9	4395
69	0.40	1.6	0.05	1	NB (86)	-	50	90	5.2	6930

Polymer properties

Example	Mn	Mw	PDI	Co-M mol%	Example	Mn	Mw	PDI	Co-M mol%
62	303742	992944	3.3	2.4	66	258724	750300	2.9	10.1
63	79500	204500	2.6	1.4	67	300961	879940	2.9	15.5
64	22400	55000	2.5	4.5	68	266707	584906	2.2	23.5
65	95800	239600	2.5	0.4	69	135379	424320	3.1	27.4

Note 1

- 5 ETA = ethyl trichloroacetate- C₂H₅OC(O)CCl₃

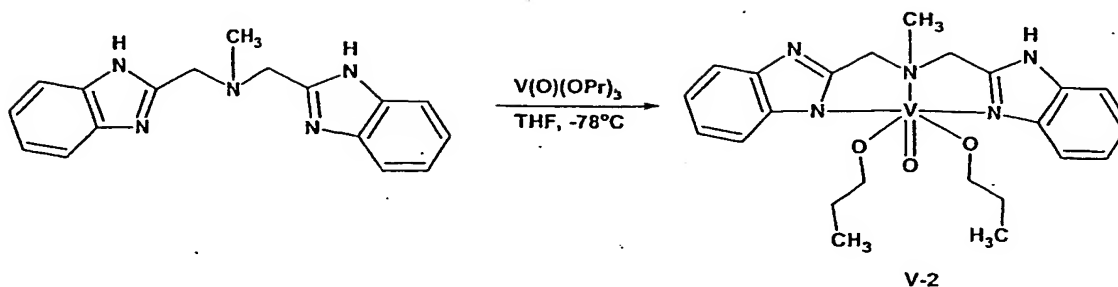
Note 2

C₃H₆ = propene; 1-H = 1-hexene; NB = norbornene (2,2,1-bicyclohept-2-ene).

Note 3 - Temperature left uncontrolled during the polymerisation reaction. The change is due to the heat formation during the polymerisation reaction.

- 10 Example 70

[*N,N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine]dipropoxyxovanadium(V) (V-2)



A cooled to -78°C solution of 0.42 g (1.72 mmol) tripropoxyoxovanadium (V) in 10 ml THF was added to a cold (-78°C) slurry of [N,N-bis(1H-benzimidazol-2-ylmethyl)-N-methylamine] in 20 ml THF. The mixture was allowed to warm up to room temperature and stirred for 30 min. The orange-red solution was filtered to remove any traces of insoluble materials (ligand) and the filtrate evaporated to c.a. 5 ml. Addition of 50 ml pentane resulted in the formation of an orange solid which was filtered, washed with 2 x 5 ml pentane and dried under reduced pressure. Yield – 0.72g (88.0%). Microanalysis, %: Calculated for $\text{C}_{23}\text{H}_{30}\text{N}_5\text{O}_3\text{V}$: C 58.10, H 6.36, N 14.73. Found: C 57.93, H 6.26, N 14.77. ^1H NMR (250 MHz, $\text{D}^2\text{-DCM}$), δ : 0.85 (t, $J_{\text{HH}} = 14.7$ Hz 6H), 1.62 (m, 4H), 2.85 (s, 3H), 3.08 (d, $J_{\text{HH}} = 15.9$ Hz 2H), 4.02 (d, $J_{\text{HH}} = 16.2$ Hz, 2H), 4.88 (dt, $J_{\text{HH}} = 13.4$ Hz, $J_{\text{HH}} = 11.6$ Hz, 2H), 5.34 (dt, $J_{\text{HH}} = 12.5$ Hz, $J_{\text{HH}} = 11.3$ Hz, 2H), 7.14 (m, 4H), 7.42 (m, 2H), 8.05 (m, 2H). ^{51}V NMR [131 MHz, $\text{V}(\text{O})\text{Cl}_3$, $\text{d}^2\text{-DCM}$], δ , ppm: -560.2.

The crystal structure of V-2 is shown in Figure 15.

Examples 71-77

Ethylene homopolymerisation with V-2

The ethylene homopolymerisation tests were carried out using a procedure similar to that described in Example 48-61

Table V-2H-FP. Polymerisation in toluene; Fisher-Porter glass reactor

Table V-2H-FP

Ex	Cat., μmol Note 1	Me_2AlCl mmol	ECA mmol Note 2	C_2H_4 bar	H_2 bar	T $^\circ\text{C}$ Note 3	Time min	PE g	Activity g mmol^{-1} $\text{h}^{-1} \text{bar}^{-1}$
71	0.43	1.0	0.04	4	-	50-74	15	7.8	18140
72	0.10	0.05	0.03	4	1	50-62	30	8.3	41500
73	0.10	0.05	0.03	4	1	50-67	30	9.5	47500
74	0.10	0.05	0.03	4	1	50-62	30	8.6	43000

Note 1 Example 72, activated catalyst solution aged for 2 hours; Example 73, activated catalyst solution aged for 7 hours; Example 74, activated catalyst solution aged for 27 hours.

5 Note 2 ECA = ethyl trichloroacetate - $\text{C}_2\text{H}_5\text{OC}(\text{O})\text{CCl}_3$

Note 3 Temperature left uncontrolled during the polymerisation reaction. The change is due to the heat formation during the polymerisation reaction.

Polymer properties

Example	Mn	Mw	PDI
71	313121	984909	3.15

10 Table V-2H-SS. Polymerisation in heptane; Stainless steel reactor

Ex	Cat., μmol	Me_2AlCl mmol Note 1	ECA mmol Note 2	C_2H_4 Bar	H_2 bar	T, $^\circ\text{C}$	Time min	PE g	Activity g mmol^{-1} $\text{h}^{-1} \text{bar}^{-1}$
75	0.20	0.50	0.04	4	0.2	50	60	12.0	12857
76	0.10	1.00	0.04	4	0.2	70	60	6.0	15000
77	0.10	1.00	0.04	4	0.3	60	60	14.5	36250

Note 1 Me_2AlCl = dimethylaluminium chloride – DMAC; the amount of Me_2AlCl shown includes the amount of the scavenger (0.5 mmol)

Note 2 ECA = ethyl trichloroacetate - $\text{C}_2\text{H}_5\text{OC}(\text{O})\text{CCl}_3$

Polymer properties

Example	Mn	Mw	PDI		Ex	Mn	Mw	PDI
76	139684	338303	2.42		77	224724	536642	2.39

Figures 16 and 17, respectively, show ethylene uptake as a function of time for Examples 77 and 78.

5 Examples 78-81

Ethylene copolymerisation with V-2

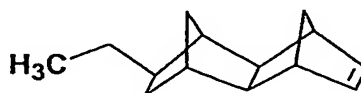
The ethylene copolymerisation tests were carried out using a procedure similar to that described in Example 48 - 61. The required amounts of comonomer were preloaded in the polymerisation reactor.

10 Table V-2C-FP. Polymerisation in toluene. Fisher-Porter glass reactor.

Ex	Cat., μmol	Me ₂ Al Cl mmol	ECA mmol Note 1	C ₂ H ₄ bar	Co-M mmol Note 2	H ₂ bar	T °C	Time min	Yield g	Activity g mmol ⁻¹ h ⁻¹ bar ⁻¹
78	0.1	0.7	0.03	4.0	NB (7.0)	-	50- 65	15	6.0	60000
79	0.40	0.8	0.04	0.5	NB (60)	-	50	60	4.5	22500
80	0.09	0.8	0.04	4.0	1,9DD (27)	-	50- 59	60	10.3	28610
81	0.40	1.0	0.04	3.0	EDE (27)	-	50- 59	30	6.5	10830

Note 1 ETA = ethyl trichloroacetate- C₂H₅OC(O)CCl₃

Note 2 NB = norbornene (2,2,1-bicyclohept-2-ene); 1,9DD = 1,9-decadiene; EDE = 8-ethyltetracyclo-[4.4.0.12,5.17,10]-3-dodecene

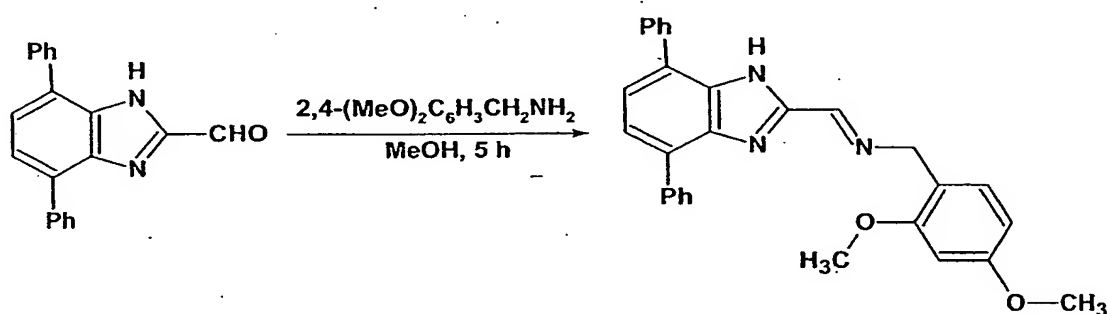


Polymer properties

Example	Mn	Mw	PDI	Co-M mol%
78	351321	983700	2.8	1.2
79	57128	143678	2.5	32.5
81	263040	631300	2.4	3.5

Example 86

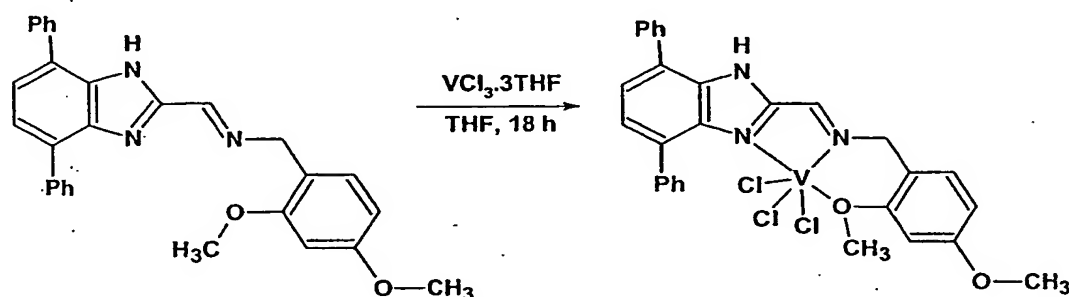
Preparation of *N*-(2,4-dimethoxybenzyl)-*N*-[(1*E*)-(4,7-diphenyl-1*H*-benzimidazol-2-yl)methylene]-amine (L-9)



A mixture of 0.11 g (0.37 mmol) 4,7-diphenyl-1*H*-benzimidazole-2-carbaldehyde and 56 mg 2,4-dimethoxybenzylamine in 3 ml methanol was stirred at room temperature for 5 hours. The yellow precipitate was filtered, washed with cold (-20°C) methanol (3 x 1 ml) and dried under reduced pressure. Yield – 0.1 g (60.1 %).

Example 87

Preparation of {*N*-(2,4-dimethoxybenzyl)-*N*-[(1*E*)-(4,7-diphenyl-1*H*-benzimidazol-2-yl)methylene]-amine} trichlorovanadium (III) (V -3)



A solution of 81 mg (0.2 mmol) *N*-(2,4-dimethoxybenzyl)-*N*-[(1*E*)-(4,7-diphenyl-1*H*-benzimidazol-2-yl)methylene]amine and 64 mg (0.2 mmol) tris(tetrahydrofuran)vanadium trichloride in 5-6 ml THF was heated at reflux for 10 min, allowed to cool down and stirred at room temperature for 18 hours. The resulted slurry was mixed with 50 ml pentane and the formed precipitate filtered, washed with pentane (2 x 2 ml) and dried under reduced pressure. Yield – 75 mg (68.9 %).

Examples 88-90

Ethylene homo- and copolymerisation with V-3

The ethylene copolymerisation tests were carried out using a procedure similar to that described in Example 48 - 61. The required amounts of comonomers were preloaded in the polymerisation reactor.

Table V-3HC-FP. Polymerisation in toluene. Fisher-Porter glass reactor.

Ex	Cat., μmol	Me ₂ Al Cl mmol	ECA mmol Note 1	C ₂ H ₄ bar	Co-M (mmol) Note 2	H ₂ bar	T °C	Time min	Yield G	Activity g mmol ⁻¹ h ⁻¹ bar ⁻¹
88	0.72	1.0	0.04	4	-	-	20-62	15	7.2	10000
89	0.43	1.0	0.04	3	1-H (81)	-	50-65	30	5.7	8740
90	0.56	1.0	0.04	3	NB (36)	-	50-70	10	8.0	28600

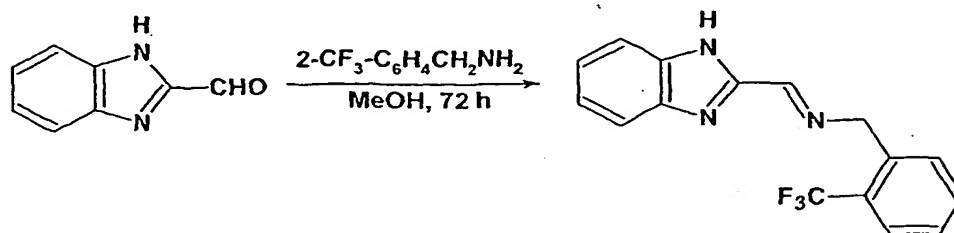
Note 1 ETA = ethyl trichloroacetate- C₂H₅OC(O)CCl₃

Note 2 NB = norbornene (2,2,1-bicyclohept-2-ene); 1-H = 1-hexene Polymer properties

Example	Mn	Mw	PDI	NB mol%	1-H mol%
88	655100	1722600	2.63	-	-
89	123200	299300	2.43	-	1.1
90	135991	737242	5.42	12	-

Example 91

Preparation of *N*-[(1*E*)-1*H*-benzimidazol-2-ylmethylene]-*N*-[2-(trifluoromethyl)benzyl]amine (L-10)



5

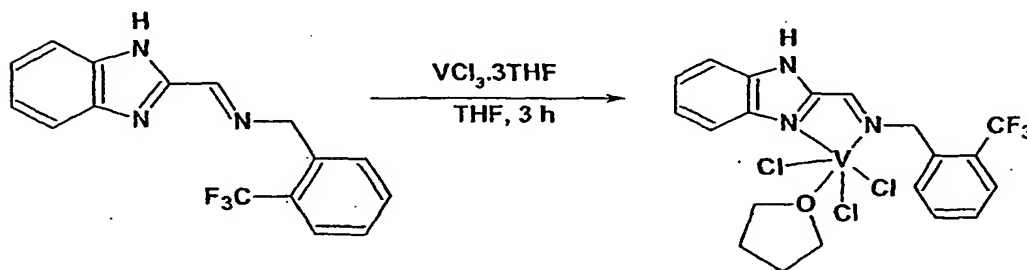
A mixture of 1.1 g (7.5 mmol) 1*H*-benzimidazole-2-carbaldehyde (Fluorochem), 1.3 g (7.5 mmol) 2-trifluoromethylbenzylamine and 1 drop glacial acetic acid in 10 ml methanol was stirred at room temperature for 72 hours. The resulted yellow solution was evaporated to c.a. 2-3 ml, cooled to -40°C and the formed solid filtered. It was washed with methanol/water mixture (1/2) and dried under reduced pressure. Yield – 1.96 g (86.4%). ^1H NMR (250 MHz, D_2O -DCM), δ : 5.03 (s, 2H), 7.28-7.69 (m, 8H), 8.46 (s, 1H).

10

Example 92

Preparation of {*N*-[(1*E*)-1*H*-benzimidazol-2-ylmethylene]-*N*-[2-(trifluoromethyl)benzyl]amine} tetra-hydrofuranotrichlorovanadium (III) (V-4)

15



20

A mixture of 0.40 (1.3 mmol) g *N*-[(1*E*)-1*H*-benzimidazol-2-ylmethylene]-*N*-[2-(trifluoromethyl)-benzyl]amine and 0.52 g (1.3 mmol) tris(tetrahydro-furan)vanadium trichloride in 40 ml THF was stirred at room temperature for 3 hours. The volume of the reaction mixture was then reduced to c.a. 10 ml and 70 ml pentane were added. The

formed precipitate was filtered, washed with 3 x 5 ml pentane and dried under reduced pressure. Yield – 0.62 g (89.6%).

Examples 93-94

Ethylene homo- and copolymerisation with V-4

- 5 The ethylene copolymerisation tests were carried out using a procedure similar to that described in Example 48 - 61. The required amounts of comonomers were preloaded in the polymerisation reactor.

Table V-4HCT-FP. Polymerisation in toluene. Fisher-Porter glass reactor.

Ex	Cat., μmol	Me ₂ Al Cl mmol	ECA mmol Note 1	C ₂ H ₄ bar	Co-M (mmol) Note 2	H ₂ bar	T °C	Time min	Yield G	Activity g mmol ⁻¹ h ⁻¹ bar ⁻¹
93	0.37	1.0	0.04	4	-	-	20- 72	30	8.0	10800
94	0.32	1.0	0.05	3	NB (36)	-	50- 70	15	9.3	38750

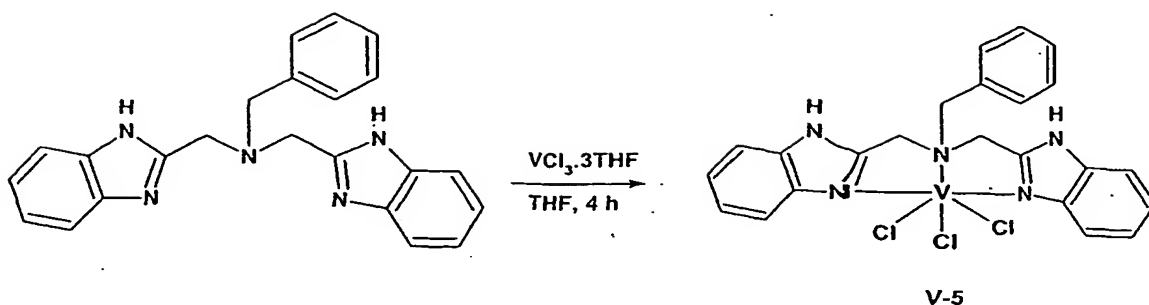
Note 1 ETA = ethyl trichloroacetate- C₂H₅OC(O)CCl₃

- 10 Note 2 NB = norbornene (2,2,1-bicyclohept-2-ene).

Polymer Properties					
Example	Mn	Mw	PDI	NB mol%	1-H mol%
93	Insoluble	insoluble	-	-	-
94	-	-	-	14.0	-

Example 96

Preparation of {N,N-bis(1*H*-benzimidazol-2-ylmethyl)-N-benzylamine} trichlorovanadium (III) (V-5)



Analogously to Example 48, [N,N-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-benzylamine]-trichlorovanadium(III) (V-1) from 1.0 g (2.7 mmol) N,N-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-benzylamine, 1.0 g (2.8 mmol) tris(tetrahydrofuran)vanadium trichloride and 40 ml THF. Yield 1.40 g (97.5 %). Microanalysis, %. C₂₃H₂₁N₅Cl₃V: C 52.64, H 4.0.3, N 13.35. Found: C 52.50, H 4.14, N 13.15. $\mu_{\text{eff.}} = 2.89 \text{ BM}$.

Example 97

Ethylene homopolymerisation with V-5

The ethylene polymerisation tests were carried out using a procedure similar to that described in Example 48 - 61.

Table V-5H-FP. Polymerisation in toluene. Fisher-Porter glass reactor.

Ex	Cat., μmol	Me ₂ Al Cl mmol	ECA mmol Note 1	C ₂ H ₄ bar	H ₂ L	T °C	Time min	Yield g	Activity g mmol ⁻¹ h ⁻¹ bar ⁻¹
97	0.09	0.6	0.08	4.8	0.2	60- 66	30	5.1	23610

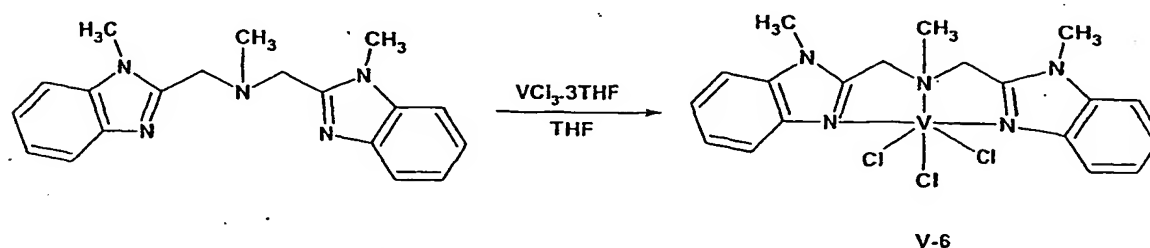
Note 1 ETA = ethyl trichloroacetate- C₂H₅OC(O)CCl₃

Polymer properties

Example	Mn	Mw	PDI
97	71547	172940	2.4

Example 98

Preparation of {*N*-methyl-*N,N*-bis[(1-methyl-1*H*-benzimidazol-2-yl)methyl]amine} trichloro-vanadium(III) (V-6)



5

Analogously to Example 18 {*N*-methyl-*N,N*-bis[(1-methyl-1*H*-benzimidazol-2-yl)methyl]-amine} trichlorochromium (III) from 0.3 g (0.94 mmol) *N*-methyl-*N,N*-bis[(1-methyl-1*H*-benzimidazol-2-yl)methyl]amine, 0.35 g (0.94 mmol) tris(tetrahydrofuran)vanadium trichloride and 20 ml THF. Yield 0.30 g (67.0%).

10 Microanalysis, %. $C_{19}H_{21}N_5Cl_3V$: C 47.87, H 4.44, N 14.69. Found: C 47.62, H 4.46, N 14.56

Example 99

Ethylene homopolymerisation with V-6

The ethylene polymerisation tests were carried out using a procedure similar to that

15 described in Example 48 - 61.

Table V-6H-FP. Polymerisation in toluene. Fisher-Porter glass reactor.

Exa mpl e	Cat., μmol	Me_2AlCl mmol	ECA mmol Note 1	C_2H_4 bar	H_2 L	T $^{\circ}\text{C}$	Time min	Yield g	Activity $\text{g mmol}^{-1}\text{h}^{-1}\text{bar}^{-1}$
99	0.07	0.4	0.08	4.8	0.2	60- 63	55	2.3	7467

Note 1 ETA = ethyl trichloroacetate- $\text{C}_2\text{H}_5\text{OC}(\text{O})\text{CCl}_3$

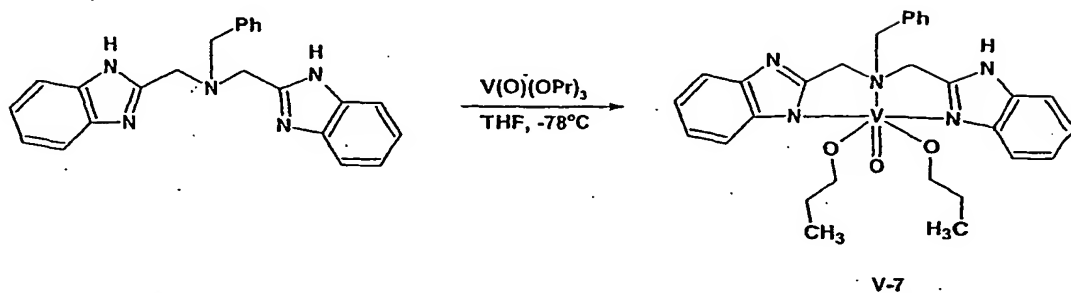
Polymer properties

Example	Mn	Mw	PDI
99	144595	441768	3.1

Example 100

Preparation of [N,N-bis(1H-benzimidazol-2-ylmethyl)-N-

5 benzylamine]dipropoxyxovanadium(V) (V-7)



A cooled to -78°C solution of 1.65 g (6.8 mmol) tripropoxyxovanadium (V) in 10 ml THF was added to a cold (-78°C) slurry of [N,N-bis(1H-benzimidazol-2-ylmethyl)-N-benzylamine] (2.50 g, 6.8 mmol) in 30 ml THF. The mixture was allowed to warm up to room temperature and stirred for 30 min. The filtrate was evaporated to c.a. 10 ml. The formed orange precipitate was filtered, washed with 2 x 10 ml pentane and dried under reduced pressure. Yield – 1.1g (29.2.0%). ^1H NMR (250 MHz, $\text{D}^2\text{-DCM}$), δ : 0.91 (t, $J_{\text{HH}} = 14.9$ Hz 6H), 1.69 (m, 4H), 2.93 (d, $J_{\text{HH}} = 15.5$ Hz 2H), 4.25 (d, $J_{\text{HH}} = 15.6$ Hz, 2H), 4.52 (s, 2H), 4.98 (m, 2H), 5.41 (m, 2H), 7.01 (m, 11H), 7.94 (d, $J_{\text{HH}} = 7.9$ Hz, 2H), 8.05.

Example 101

Ethylene homopolymerisation with V-7

The ethylene polymerisation tests were carried out using a procedure similar to that described in Example 48 – 61

Table V-7H-SS. Polymerisation in heptane. Stainless steel reactor.

Ex	Cat., μmol	Me_2AlCl l mmol	ECA mmol Note 1	C_2H_4 bar	H_2 bar	T $^\circ\text{C}$	Time min	Yield g	Activity g mmol^{-1} $\text{h}^{-1} \text{bar}^{-1}$
101	0.14	0.5	0.04	4.0	0.2	60	60	8.9	15892

Note 1 ETA = ethyl trichloroacetate- $\text{C}_2\text{H}_5\text{OC}(\text{O})\text{CCl}_3$

Example 102

Preparation of supported on silica catalyst V-2. (V-2-SiO₂)

- 5 To a slurry of 15 g silica 948, calcined at 250°C for 5h) in 150 ml toluene was added a solution 15 mg [*N,N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine]dipropoxyoxovanadium(V) (Example 70) dissolved in 100 ml toluene. The slurry was stirred at room temperature for 30 min, filtered, washed with pentane (3 x 100 ml) and dried at 40°C under vacuum. Thus prepared the solid catalyst contains 2.1 $\mu\text{mol V / SiO}_2$.

10 Example 103

Ethylene homopolymerisation with V-2-SiO₂

The ethylene polymerisation tests were carried out using a procedure similar to that described in Example 48 - 61. The solid catalyst was preactivated and transferred in the reactor via cannula .

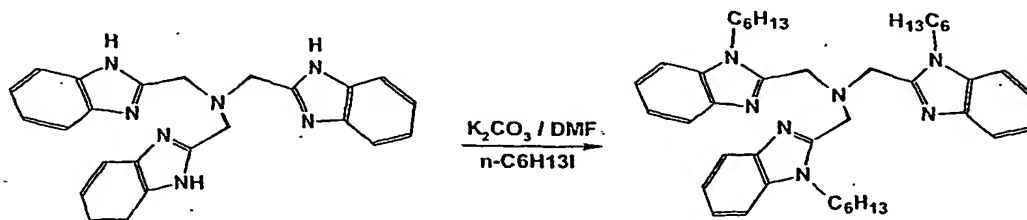
15

Table V-2-SiO₂H-FP. Polymerisation in toluene. Fisher-Porter glass reactor.

Ex	Cat., μmol	Me_2AlCl Cl Mmol	ECA mmol Note 1	C_2H_4 bar	H_2 L	T $^\circ\text{C}$	Time min	Yield g	Activity g mmol^{-1} $\text{h}^{-1} \text{bar}^{-1}$
103	1.1	2.0	0.07	4	-	60- 75	15	5.0	4545

Note 1 ETA = ethyl trichloroacetate- $\text{C}_2\text{H}_5\text{OC}(\text{O})\text{CCl}_3$

Example 104

Preparation of N,N,N-tris[1-hexyl-1*H*-benzimidazol-2-yl)methyl]amine

A mixture of 2g (4.9 mmol) N,N,N-tris(1*H*-benzimidazol-2-yl)methylamine, 10 g
 5 anhydrous K₂CO₃, 20 ml DMF and 3.1 g (14.7 mmol) n-hexyliodide was stirred at room
 temperature for 48 hours. A volume of 200 ml water was added and the resulting
 mixture was intensively stirred for 30 min. The formed precipitate was filtered, washed
 with excess of water and dried at 60°C under reduced pressure. Recrystallisation from n-
 heptane gave 2g (62 %) of the product. 1H NMR (250 MHz, CDCl₃), δ, ppm: 0.44 (m,
 10 6H), 0.73 (t, 9H), 0.82 (m, 6H), 0.97 (m, 6H), 1.14 (m, 6H), 3.42 (t, 6H), 4.22 (s, 6H),
 7.22 (m, 9H), 7.74 (m, 3H).

Example 105

{N,N,N-tris[1-hexyl-1*H*-benzimidazol-2-yl)methyl]amine} dichlorochromium (III)
 15 chloride (Cr-9)

Similarly to {[N,N,N-tris(1*H*-benzimidazol-2-yl)methyl]amine}dichlorochromim (III)-
 chloride from CrCl₃.3THF and N,N,N-tris[1-hexyl-1*H*-benzimidazol-2-
 yl)methyl]amine}.

Yield – 54%.

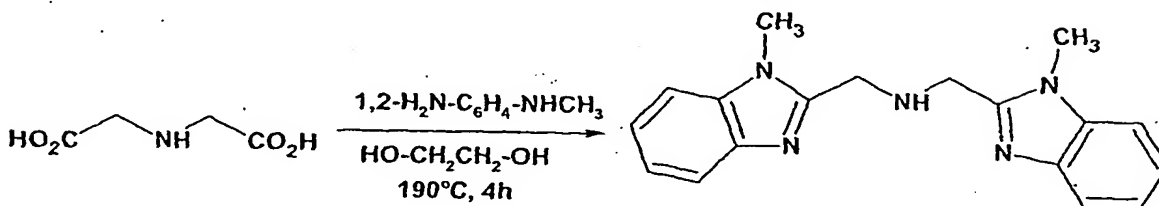
20 Example 106

Ethylene oligomerisation/polymerisation test with Cr-9

Ex	Cat., μmol	MAO, mmol	Temp. Setpoint, °C	P C ₂ H ₄ bar	Pol. time, min	ΔT, deg.	Soluble fraction g	Insoluble fraction g	Activity, g/mmol. h.bar
106	20	1.0	22	4	60	-	-	3.4	43

Polymer properties

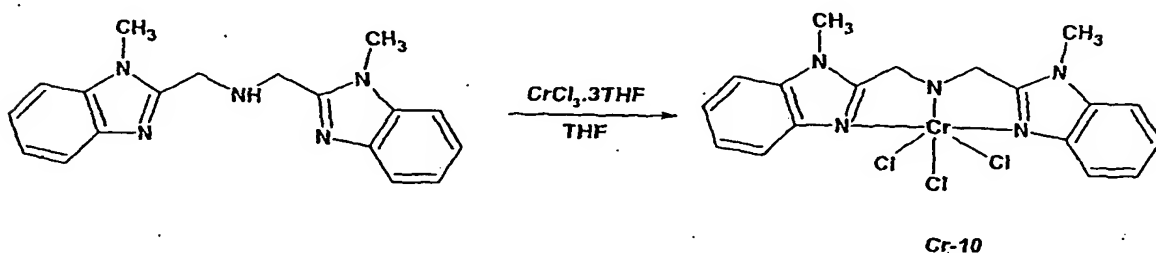
Example	M _n	M _w	PDI
99	15000	197000	13

Example 107Preparation of N,N-bis[(1-methyl-1*H*-benzimidazol-2-yl)methyl]amine

A mixture of 2.7 g (20.3 mmol) methyliminodiacetic acid and 5.0 g (40.6 mmol) N-methyl-o-phenylene diamine in 20-30 ml ethylenediol was stirred at 190°C for 4 hours. After cooling to room temperature, the reaction mixture was mixed with 100-120 ml
 10 water and stirred for 15 minutes. The solid was filtered, washed with water (3 x 20 ml) and dried at 60°C under reduced pressure. Yield – 3.5 g (56%). The compound can be recrystallised from a methanol/water mixture.

Example 108

{N,N-bis[(1-methyl-1*H*-benzimidazol-2-yl)methyl]amine} trichlorochromium (III) (Cr-
 15 10)



Similarly to [N,N-bis(1*H*-benzimidazol-2-ylmethyl)-N-methylamine]trichloro-
 chromium(III) (Cr-1) from 0.5 g (1.64 mmol) N,N-bis[(1-methyl-1*H*-benzimidazol-2-
 20 yl)methyl]amine, 0.61 g (1.64 mmol) CrCl₃.3THF and 20 ml THF. Yield – 0.39 g (51%).

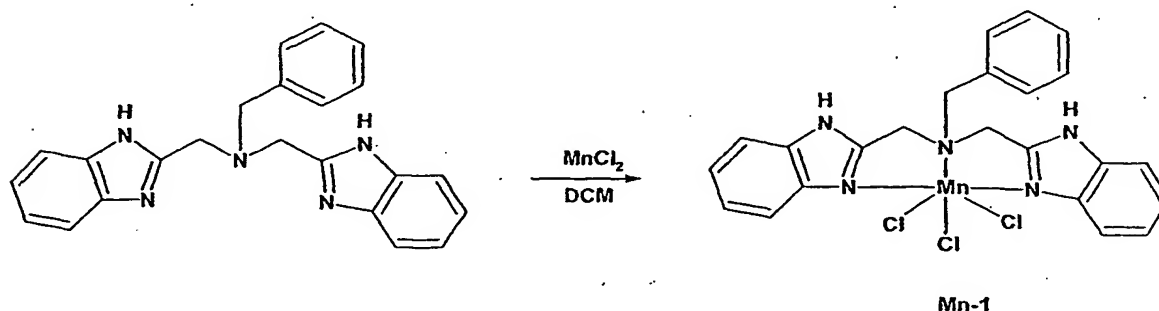
Example 109

Attempted ethylene oligomerisation/polymerisation test with Cr-10

Ex	Cat., μmol	MAO, mmol	Temp. Setpoint, °C	P C ₂ H ₄ bar	Pol. time, min	ΔT, deg.	Soluble fraction g	Insoluble fraction g	Activity, g/mmol. h.bar
109	10	1.0	20	4	60	-	inactive	inactive	inactive

Example 110

- 5 [N,N-bis(1*H*-benzimidazol-2-ylmethyl)-N-benzylamine]dichloromanganese (Mn – 1)



A mixture of 0.50 g (1.41 mmol) N,N-bis(1*H*-benzimidazol-2-ylmethyl)-N-benzylamine and 0.18 g (1.41 mmol) MnCl₂ was stirred in 10 ml refluxing DCM for 10 min. The reaction mixture was then cooled to room temperature and stirred for another 4 hours.

- 10 The pale pink precipitate was filtered, washed with 2 x 5 ml DCM and dried under reduced pressure. Yield 0.48 g (69 %).

Example 111-112

Attempted ethylene oligomerisation/polymerisation test with Mn-1

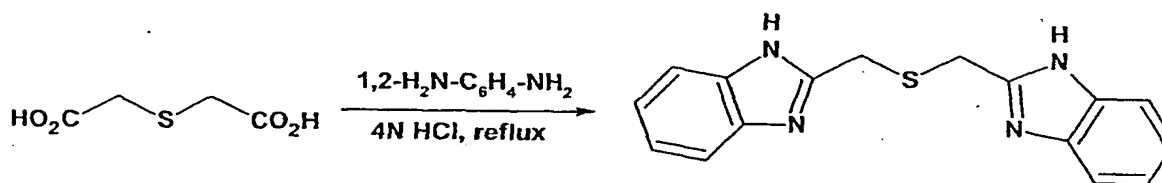
Ex	Cat., μmol	Co-Cat., (mmol) Note 1	Temp. Setpoint, °C	P C ₂ H ₄ bar	Pol. time, min	ΔT, deg.	Soluble fraction g	Insoluble fraction g	Activity, g/mmol. h.bar
111	20	TIBAL 1.0	60	4	60	-	inactive	inactive	inactive
112	20	MAO (1.0)	20	20	60	-	inactive	inactive	inactive

Note 1

TIBAL = triisobutyl aluminium

Example 113

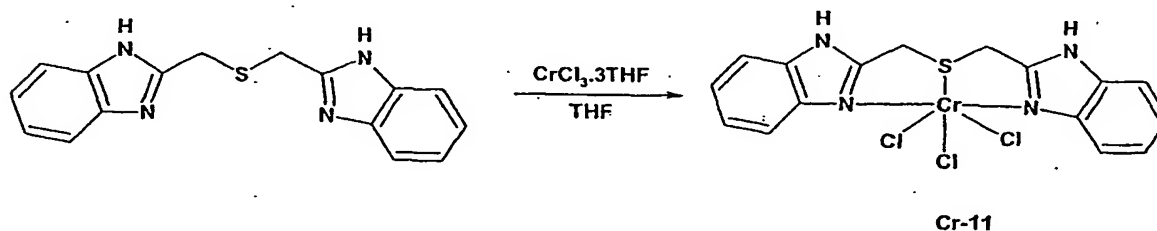
2-{[(1H-benzimidazol-2-ylmethyl)thio]methyl}-1H-benzimidazole



A solution of 4.1 g (27.3 mmol) thiodiacetic acid and 4.9 g (27.3 mmol) o-phenylene diamine in 40 ml 4N HCl was stirred at reflux for 4 hours. The reaction mixture was cooled to room temperature and neutralised with conc. NH₄OH. The formed precipitate was filtered, washed with water (3 x 40 ml) and dried under vacuum. Yield – 2.4g (25.2 %).

Example 114

{2-{[(1H-benzimidazol-2-ylmethyl)thio]methyl}-1H-benzimidazole} trichloro-chromium (III) (Cr-11)



Similarly to [N,N-bis(1H-benzimidazol-2-ylmethyl)-N-methylamine]trichloro-chromium(III) (Cr-1) from 0.25 g (0.85 mmol) 2-{[(1H-benzimidazol-2-ylmethyl)thio]methyl}-1H-benzimidazole, 0.32g (0,85 mmol) CrCl₃.3THF and 30 ml THF. Yield – 0.20 g (52.6%).

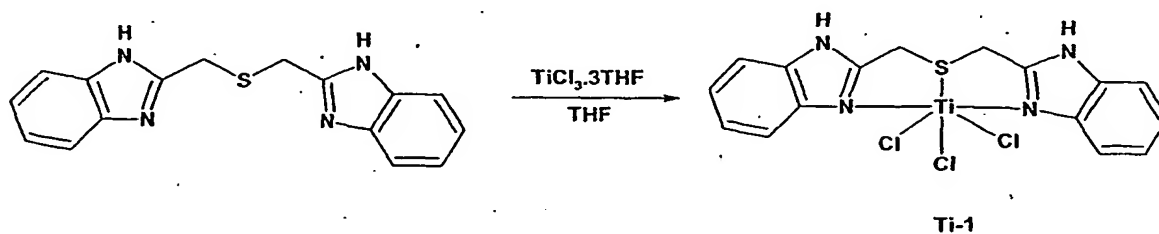
5 Example 115

Attempted ethylene oligomerisation/polymerisation test with Cr-10

Example	Cat.,	MAO,	Temp.	P	Pol.	□T,	Soluble	Insoluble	Activity,
	μmol	mmol	Setpoint, °C	C ₂ H ₄ bar	time, min	deg.	fraction g	fraction g	
115	10	1.0	20	4	60	-	inactive	inactive	inactive

Example 116

10 {2-{[(1H-benzimidazol-2-ylmethyl)thio]methyl}-1H-benzimidazole} trichlorotitanium (III) (Ti-1)



15 Similarly to [N,N-bis(1H-benzimidazol-2-ylmethyl)-N-methylamine]trichloro-chromium(III) (Cr-1) from 0.50 g (1.70 mmol) 2-{[(1H-benzimidazol-2-ylmethyl)thio]methyl}-1H-benzimidazole, 0.62g (1.70 mmol) TiCl₃.3THF and 40 ml THF. Yield – 0.41 g (54.8%).

Example 117

Ethylene polymerisation test with Ti-1

Example	Cat., μmol	MAO, mmol	Temp. Setpoint, °C	P C ₂ H ₄ bar	Pol. time, min	ΔT, deg.	Soluble fraction g	Insoluble fraction g	Activity, g/mmol.h.bar
117	20	1.0	60	1	60	-	-	1.3	65

Comparative Example 1

Ethylene homopolymerisation with tripropoxyoxovanadium (V) - (PrO)₃V=O

The ethylene polymerisation test was carried out using a procedure similar to that described in Example 48 - 61.

- 5 Table V-C1H-FP. Polymerisation in toluene. Fisher-Porter glass reactor.

Example	Cat., μmol	Me ₂ AlC l mmol	ECA mmol Note 1	C ₂ H ₄ bar	H ₂ L	T °C	Time Min	Yield g	Activity g mmol ⁻¹ h ⁻¹ bar ⁻¹
1C	20.0	1.0	0.04	4	-	50	60	-	inactive

Note 1

ETA = ethyl trichloroacetate- C₂H₅OC(O)CCl₃

Comparative Example 2

Ethylene homopolymerisation with vanadium trichloride - VCl₃

- 10 The ethylene polymerisation test was carried out using a procedure similar to that described in Example 48 - 61.

Table V-C2H-FP. Polymerisation in toluene. Fisher-Porter glass reactor.

Example	Cat., μmol	Me ₂ AlC l mmol	ECA mmol Note 1	C ₂ H ₄ bar	H ₂ L	T °C	Time Min	Yield g	Activity g mmol ⁻¹ h ⁻¹ bar ⁻¹
2C	7.5	1.0	0.04	4	-	50	15	0.6	80

Note 1

ETA = ethyl trichloroacetate- $\text{C}_2\text{H}_5\text{OC}(\text{O})\text{CCl}_3$

Comparative Example 3

Ethylene homopolymerisation with bis(cyclopentadiene)vanadiumdichloride (IV)

5 $(\text{Cp}_2\text{VCl}_2)$

The ethylene polymerisation test was carried out using a procedure similar to that described in Example 48 - 61.

Table V-C3H-FP. Polymerisation in toluene. Fisher-Porter glass reactor.

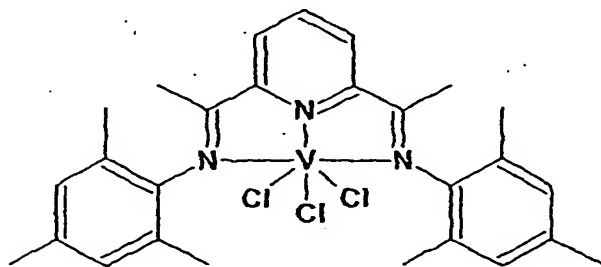
Example	Cat., μmol	Me_2AlCl l mmol	ECA mmol Note 1	C_2H_4 bar	H_2 L	T $^\circ\text{C}$	Time e Min	Yield g	Activity $\text{g mmol}^{-1} \text{h}^{-1} \text{bar}^{-1}$
3C	0.5	1.0	0.05	4	-	50-52	60	4.1	2050

Note 1

10 ETA = ethyl trichloroacetate- $\text{C}_2\text{H}_5\text{OC}(\text{O})\text{CCl}_3$

Comparative Example 4

Ethylene homopolymerisation with the following complex:



The ethylene polymerisation test was carried out using a procedure similar to that described in Example 48 - 61.

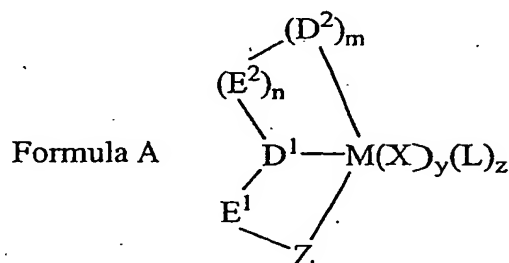
15

Table V-C1H-FP. Polymerisation in toluene. Fisher-Porter glass reactor.

Example	Cat., μmol	MAO mmol	C_2H_4 bar	H_2 L	T $^\circ\text{C}$	Time e min	Yield G	Activity $\text{g mmol}^{-1} \text{h}^{-1} \text{bar}^{-1}$
4C	0.5	2.0	1	-	50	15	0.68	2772

Claims:

1. A polymerisation catalyst comprising
 - (1) a transition metal compound having the following Formula A, and optionally
 - (2) an activating quantity of a suitable activator,

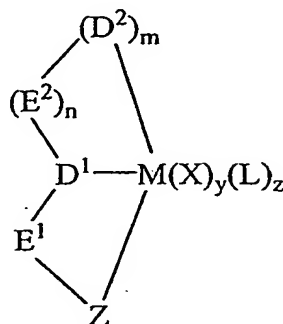


wherein Z comprises a five-membered heterocyclic group, the five membered heterocyclic group containing at least one carbon atom, at least one nitrogen atom and at least one other hetero atom selected from nitrogen, sulphur and oxygen, the remaining atoms in said ring being selected from nitrogen and carbon; M is a metal from Group 3 to 11 of the Periodic Table or a lanthanide metal; E¹ and E² are divalent groups independently selected from (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups and (vi) heterosubstituted derivatives of said groups (i) to (v); D¹ and D² are donor atoms or groups; X is an anionic group, L is a neutral donor group; n = m = zero or 1; y and z are independently zero or integers such that the number of X and L groups satisfy the valency and oxidation state of the metal M.

2. A polymerisation catalyst as claimed in claim 1 wherein the five membered

heterocyclic group contains at least 3 carbon atoms in its ring.

3. A polymerisation catalyst as claimed in claim 1 comprising
- (1) a transition metal compound having the following Formula A, and optionally
 - (2) an activating quantity of a suitable activator,



Formula A

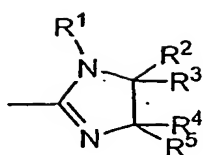
wherein Z is specifically an imidazole-containing group; M is a metal from Group 3 to 11 of the Periodic Table or a lanthanide-metal; E¹ and E² are divalent groups independently selected from (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups and (vi) heterosubstituted derivatives of said groups (i) to (v); D¹ and D² are donor groups; X is an anionic group, L is a neutral donor group; n = m = zero or 1; y and z are independently zero or integers such that the number of X and L groups satisfy the valency and oxidation state of the metal M.

4. A polymerisation catalyst as claimed in any one of Claims 1 to 3 wherein M is a metal from Group 3 to 7 of the Periodic Table or a lanthanide metal.

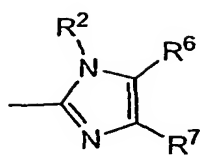
5. A polymerisation catalyst as claimed in any one of the preceding Claims wherein D¹ and / or D² are an imidazole-containing group.

6. A polymerisation catalyst as claimed in any one of Claims 3 to 5 wherein D² and Z are identical imidazole containing groups.

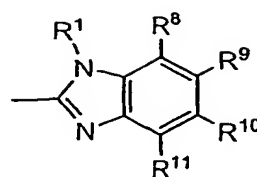
7. A polymerisation catalyst as claimed in any one of Claims 3 to 6 wherein the imidazole-containing group Z is selected from a group of Formula I, II or III



Formula I



Formula II



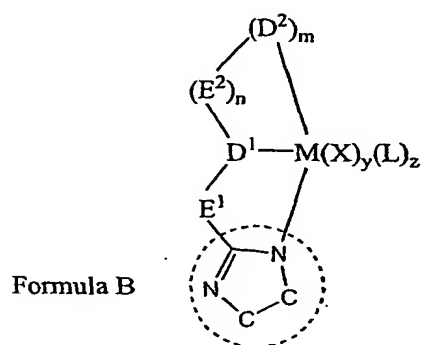
Formula III

R^1 to R^{11} are independently hydrogen or a monovalent (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic

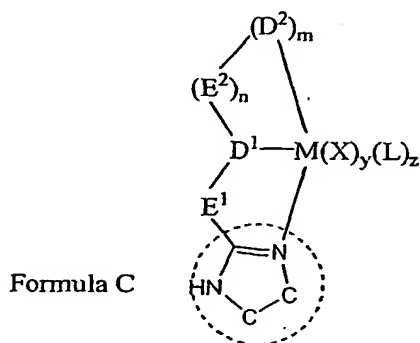
5 hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), and (vii) hydrocarbyl-substituted heteroatom groups.

8. A polymerisation catalyst as claimed in Claim 1 wherein the a transition metal compound has the following Formula B or C

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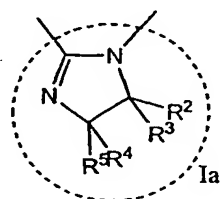
Formula B



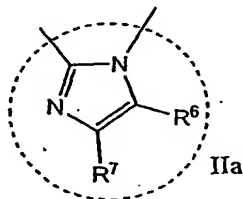
Formula C

wherein the imidazole nucleus shown within the dotted circle is selected from the divalent groups represented by the Formulae Ia, IIa, IIIa, IVa, Va and VIa,

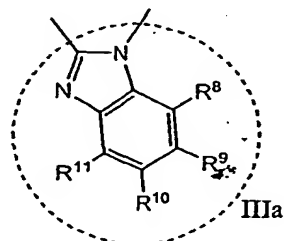
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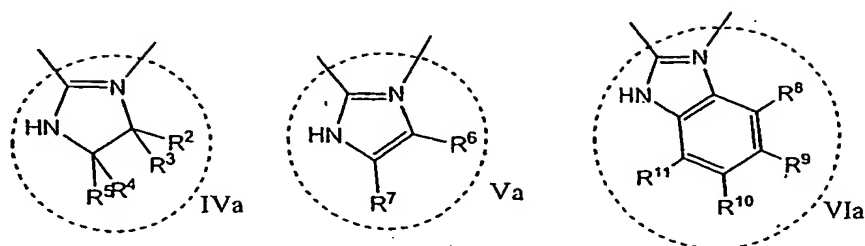
Ia



IIa



IIIa



wherein M is a metal from Group 3 to 11 of the Periodic Table or a lanthanide metal; E¹ and E² are divalent groups independently selected from (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups and (vi) heterosubstituted derivatives of said groups (i) to (v); D¹ and D² are donor groups; X is an anionic group, L is a neutral donor group; n = m = zero or 1; y and z are independently zero or integers such that the

number of X and L groups satisfy the valency and oxidation state of the metal M, wherein the groups R² to R¹¹ are independently hydrogen or a monovalent (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), and (vii) hydrocarbyl-substituted heteroatom groups.

9. A polymerisation catalyst as claimed in any one of the preceding Claims wherein E¹ and E² are independently selected from -CH₂-, -CH₂CH₂-, -CH₂CH₂CH₂-, 1,2-phenylene, *trans*-1,2-cyclopentane, *trans*-1,2-cyclohexane, 2,3-butane, 1,1'-biphenyl, 1,1'-binaphthyl, and -Si(Me)₂-.

10. A polymerisation catalyst as claimed in any one of Claims 1 to 4 or 8 wherein D¹ and D² are selected from oxygen, sulfur, an amine of formula -N(R¹²)- or a phosphine of formula -P(R¹³)- wherein R¹² and R¹³ are hydrogen or (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), (vii) hydrocarbyl-substituted heteroatom groups and (viii) an imidazole-containing group.

11. A polymerisation catalyst as claimed in any one of the preceding Claims wherein M is selected from Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W.

12. A polymerisation catalyst as claimed in any one of the preceding Claims wherein the anionic group X is selected from a halide, a hydrocarbyl group, a carboxylate, an

oxide; an amide; an alkoxide; an acetylacetonate; and a hydroxyl.

13. A polymerisation catalyst as claimed in any one Claims 1 to 11 wherein X is a non-coordinating or weakly-coordinating anion.

14. A polymerisation catalyst as claimed in any one of the preceding Claims wherein the neutral donor group L is selected from an ether, an amine, a phosphine, an olefin, water and a neutral, conjugated or nonconjugated diene,

15. A polymerisation catalyst as claimed in any one of the preceding Claims wherein the optional activator (2) is selected from organoaluminium compounds and organoboron compounds and mixtures thereof.

16. A polymerisation catalyst as claimed in Claim 15 wherein the optional activator (2) is selected from trimethylaluminium, triethylaluminium, tributylaluminium, tri-n-octylaluminium, ethylaluminium dichloride, diethylaluminium chloride, tris(pentafluorophenyl)aluminium, alumoxanes, dimethylphenylammoniumtetra(phenyl)borate, trityltetra(phenyl)borate, triphenylboron, dimethylphenylammonium tetra(pentafluorophenyl)borate, sodium tetrakis[(bis-3,5-trifluoromethyl)phenyl]borate, $H^+(OEt_2)[(bis-3,5-trifluoromethyl)phenyl]borate$, trityltetra(pentafluorophenyl)borate and tris(pentafluorophenyl) boron.

17. A polymerisation catalyst as claimed in any one of the preceding Claims wherein the optional activator is provided by a Lewis acid selected from

(a) ionic-bonding compounds having a $CdCl_2$ type or a CdI_2 type of layered crystal structure;

(b) clays, clay minerals, or ion-exchange layered compounds;

(c) heteropoly-compounds; and

(d) halogenated lanthanoid compounds.

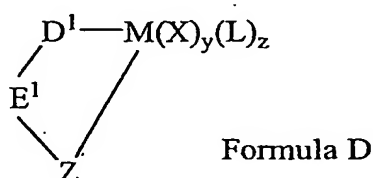
18. A polymerisation catalyst as claimed in any one of the preceding Claims wherein the optional activator is provided by a catalyst support-activator agglomerate comprising a composite of (A) at least one inorganic oxide component selected from SiO_2 , Al_2O_3 , MgO , $AlPO_4$, TiO_2 , ZrO_2 , and Cr_2O_3 and (B) at least one ion containing layered material comprising a smectite.

19. A polymerisation catalyst as claimed in any one of the preceding Claims wherein there is present a promoter comprising a halogenated organic compound.

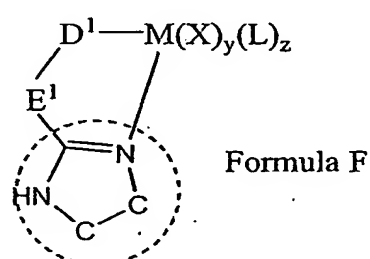
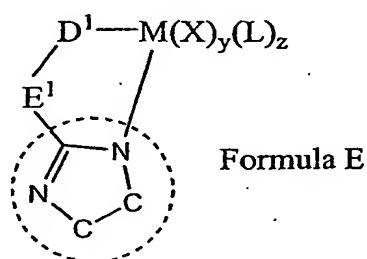
20. A polymerisation catalyst as claimed in Claim 19 wherein the promoter is selected from carbon tetrachloride, hexachloroethylene, benzylbromide, benzylchloride, ethyl trichloroacetate and 2,3- or 1,3-dichloropropylene, chloroform (CHCl_3) and n-butylchloride.

21. A polymerisation catalyst as claimed in Claim 20 wherein the transition metal is vanadium.

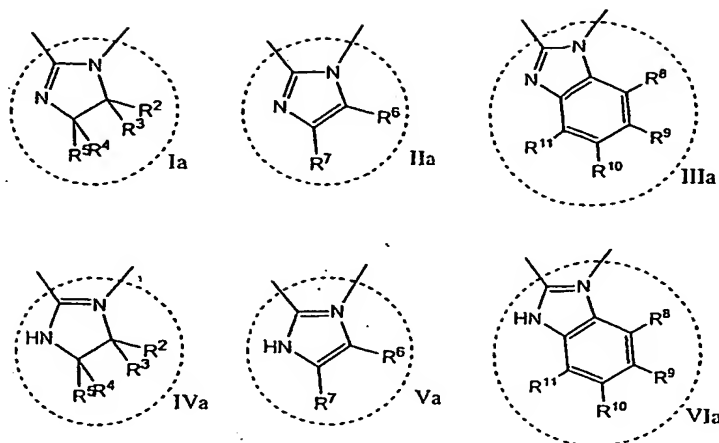
21. A polymerisation catalyst as claimed in any one of the preceding Claims wherein m and n are zero in Formula A so that the transition metal compound is of Formula D



22. A polymerisation catalyst as claimed in any one of the preceding Claims wherein m and n are zero in Formula A so that the transition metal compound is of Formula E or Formula F



and wherein the imidazole nucleus within the dotted circle is selected from the divalent groups represented by the Formulae Ia, IIa, IIIa, IVa, Va and VIa as follows:



23. A polymerisation catalyst as claimed in any one of the preceding Claims wherein in addition to the defined catalyst there is present one or more other catalysts for polymerising 1-olefins.

24. A polymerisation catalyst as claimed in any one of the preceding Claims wherein in addition to the defined catalyst there is present one or more other transition metal catalysts selected from Ziegler-Natta catalyst systems, metallocene-based catalysts, or heat activated supported chromium oxide catalysts.

25. A supported catalyst comprising the polymerisation catalyst defined in any one of the preceding Claims and a support material.

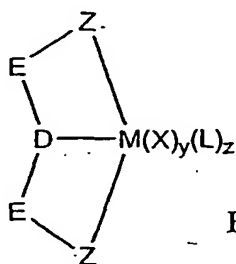
26. A process for the polymerisation and copolymerisation of 1-olefins, cycloolefins or dienes, comprising contacting the monomeric olefin under polymerisation conditions with the polymerisation catalyst claimed in any one of the preceding Claims.

27. A process as claimed in Claim 26 wherein the process is for the homopolymerisation of 1-olefins and wherein the monomer is selected from ethylene, propylene, butene, hexene, and styrene.

28. A process as claimed in Claim 26 wherein the process is for the copolymerisation of 1-olefins and wherein the monomer is selected from ethylene, propylene, 1-butene, 1-hexene, 4-methylpentene-1, octane, methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, vinyl chloride, and styrene.

29. A process as claimed in Claim 26 comprising the copolymerisation of ethylene and or propylene with comonomers selected from 1-butene, 1-hexene, 4-methylpentene-1, methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, and styrene, diene, cyclic olefin, norbornene and substituted norbornene.

30. A process as claimed in any one of Claims 26 to 29 wherein the catalyst is supported on a support material selected from silica, alumina, zirconia, talc, kieselguhr, magnesia, magnesium chloride and polymers.
31. A process as claimed in any one of Claims 26 to 30 wherein the process is carried out under gas phase, slurry phase or solution phase polymerisation conditions.
32. A process as claimed in any one of Claims 26 to 31 wherein the process is carried in the presence of hydrogen gas to modify the average molecular weight of the produced polymer.
33. A process for oligomerisation and cooligomerisation of 1-olefins, comprising contacting the monomeric olefin under oligomerisation conditions with the catalyst claimed in any one of Claims 1 to 25.
34. A polymerisation catalyst comprising
- (1) a transition metal compound having the following Formula A1, and optionally
 - (2) an activating quantity of a suitable activator,



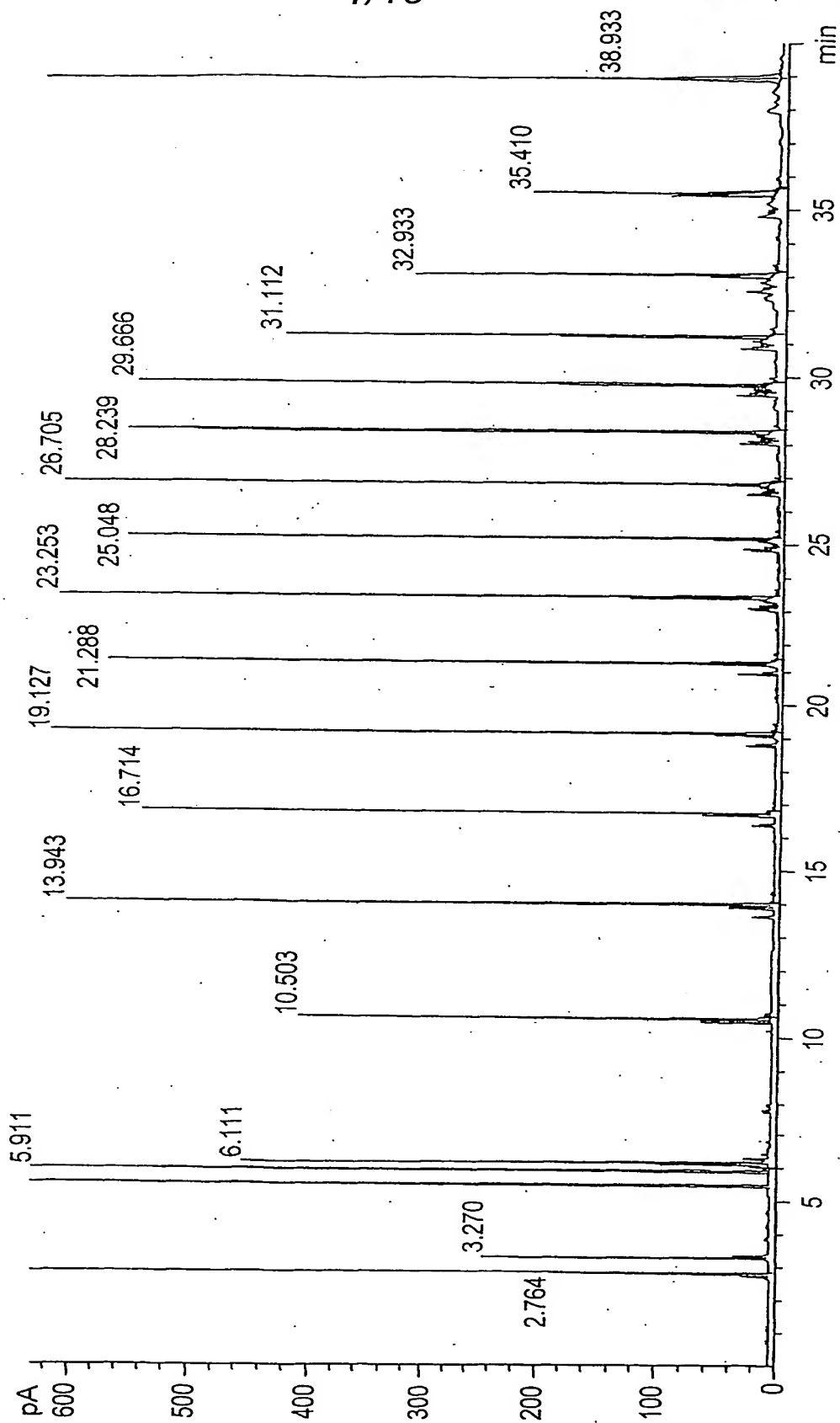
Formula A1

- wherein Z is specifically an imidazole-containing group; M is a metal from Group 3 to 7 of the Periodic Table or a lanthanide metal; E is a divalent group independently selected from (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups and (vi) heterosubstituted derivatives of said groups (i) to (v); D is a donor group; X is an anionic group, L is a neutral donor group; y and z are independently zero or integers such that the number of X and L groups satisfy the valency and oxidation state of the metal M.

1/15

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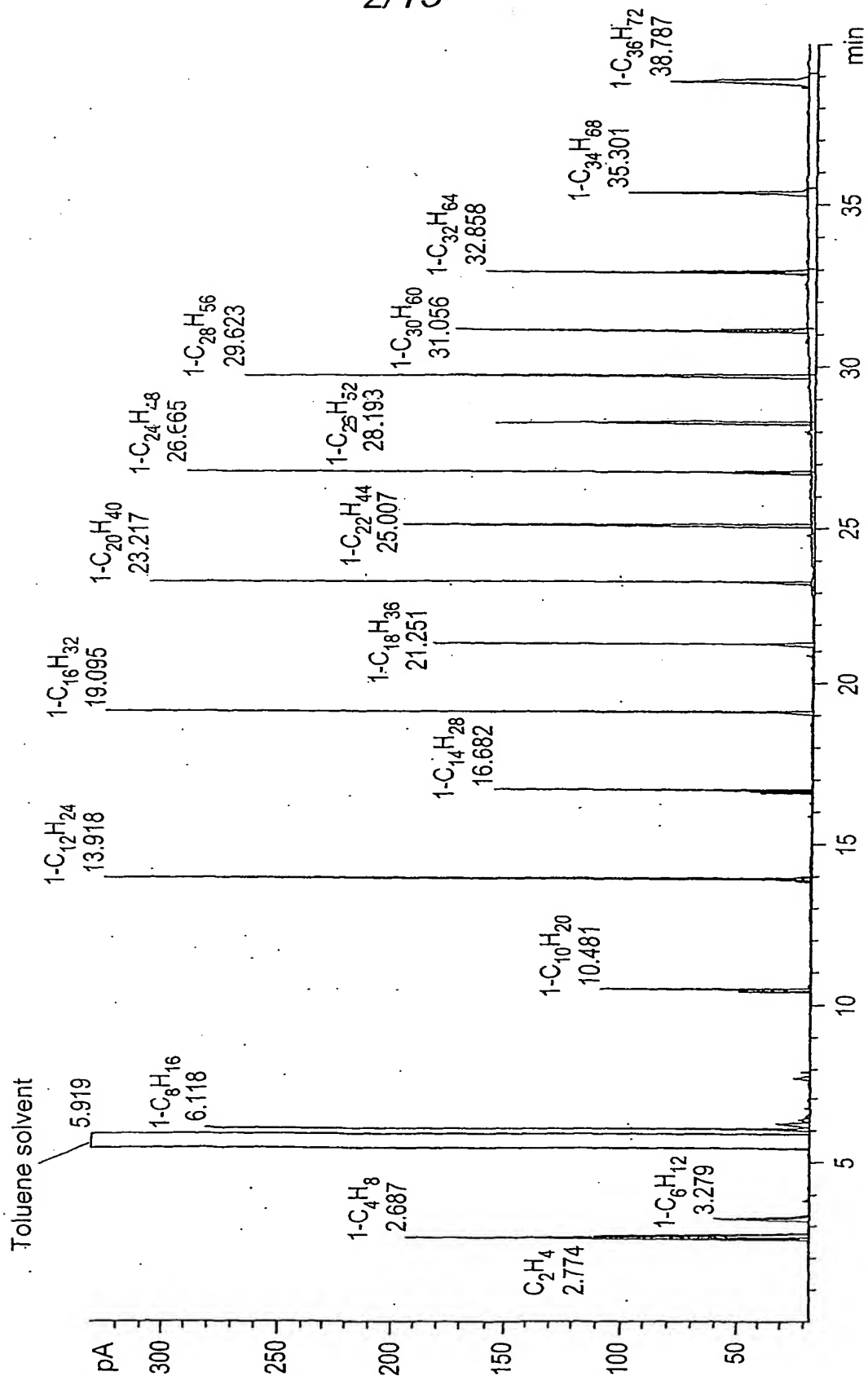
Fig.1 (Example 3)



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2/15

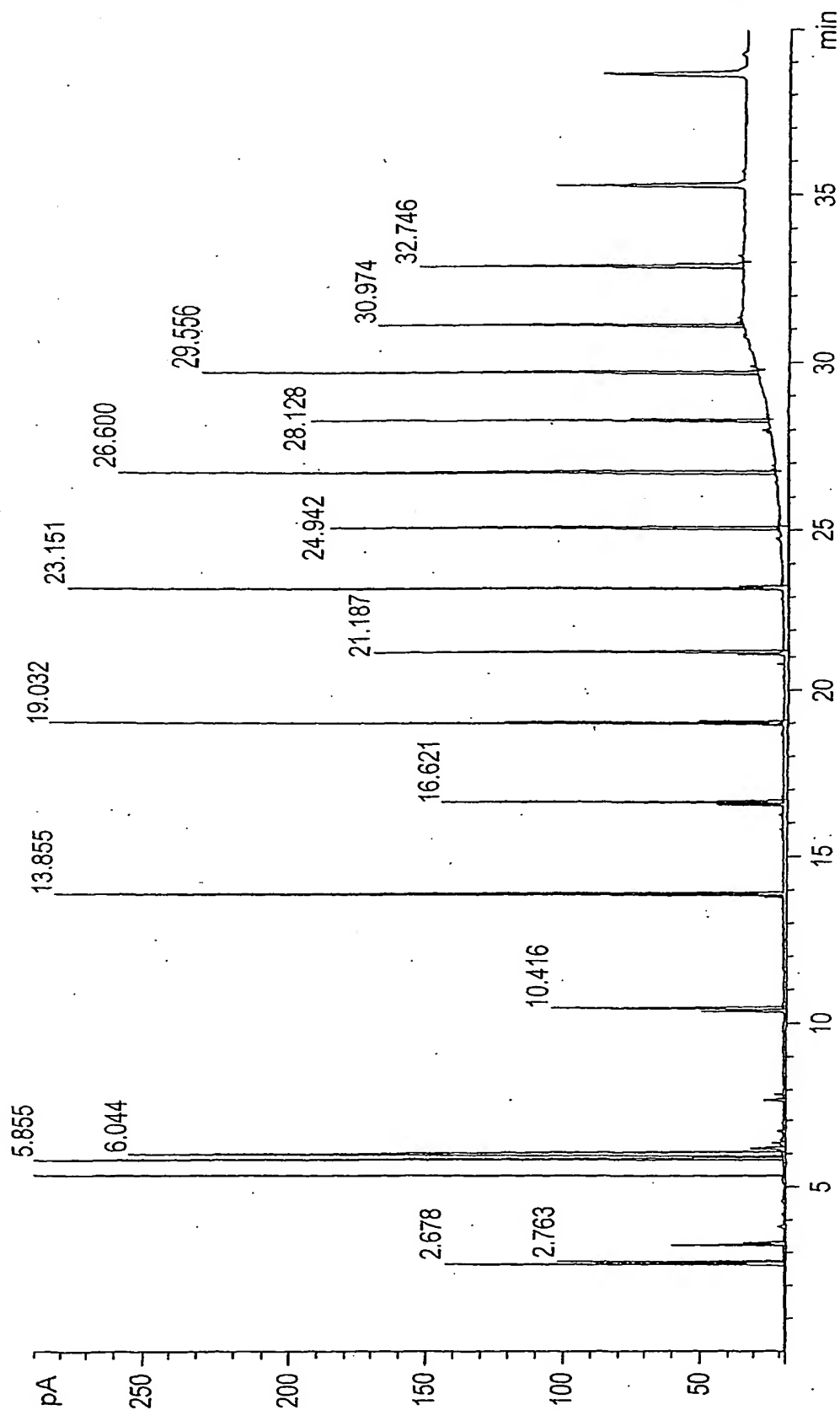
Fig.2 (Example 7)



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3/15

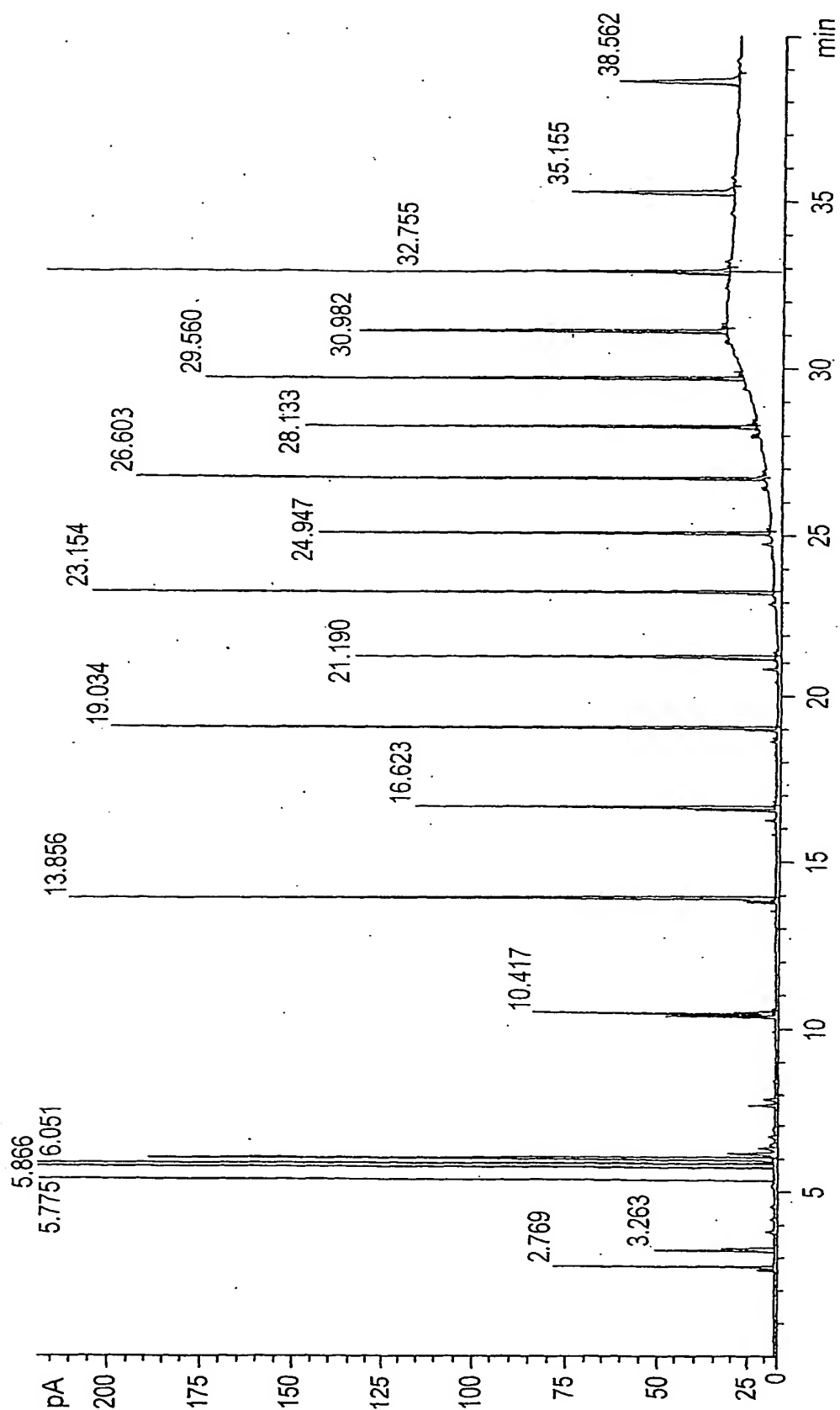
Fig.3 (Example 8)



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4/15

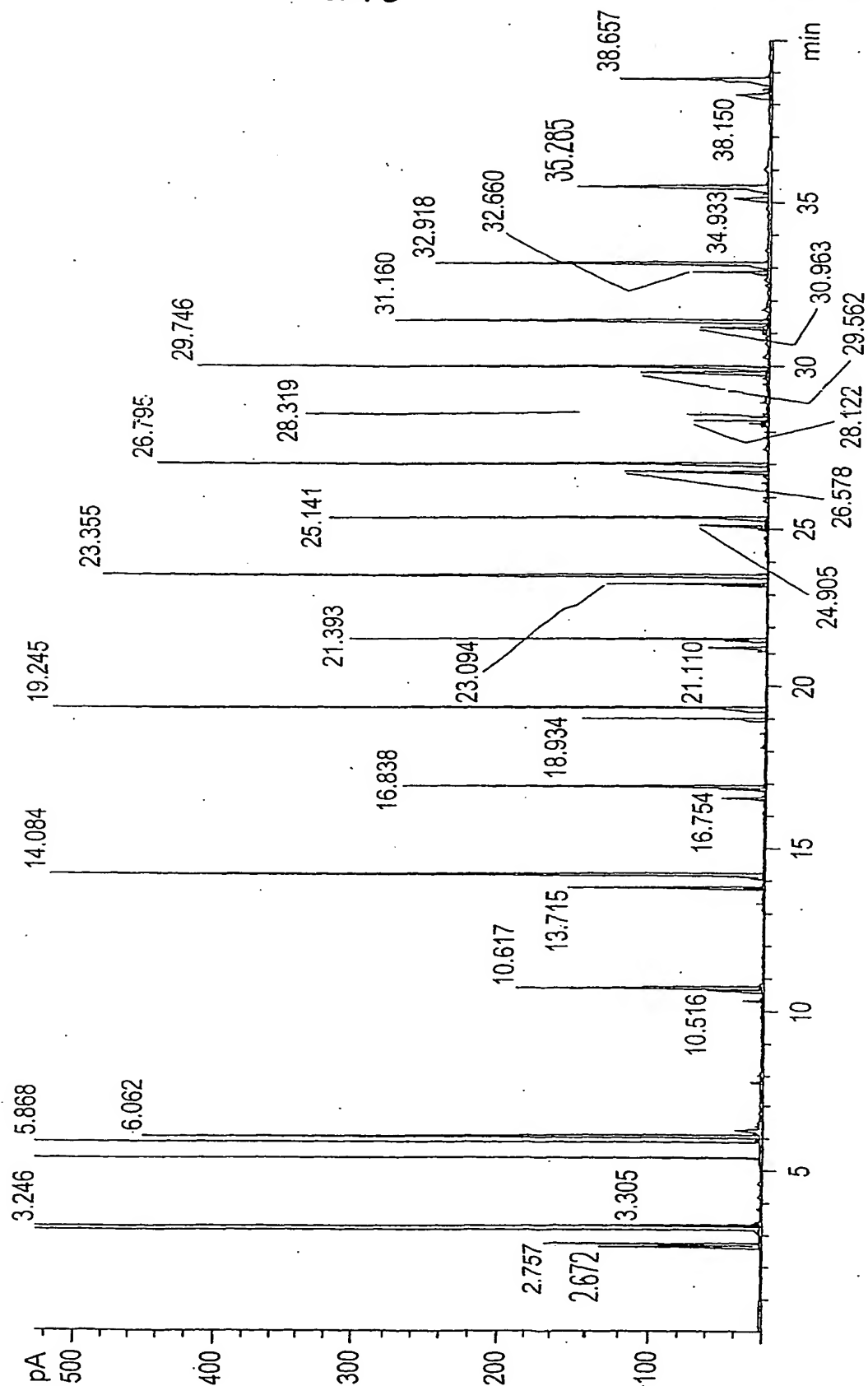
Fig.4 (Example 9)



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5/15

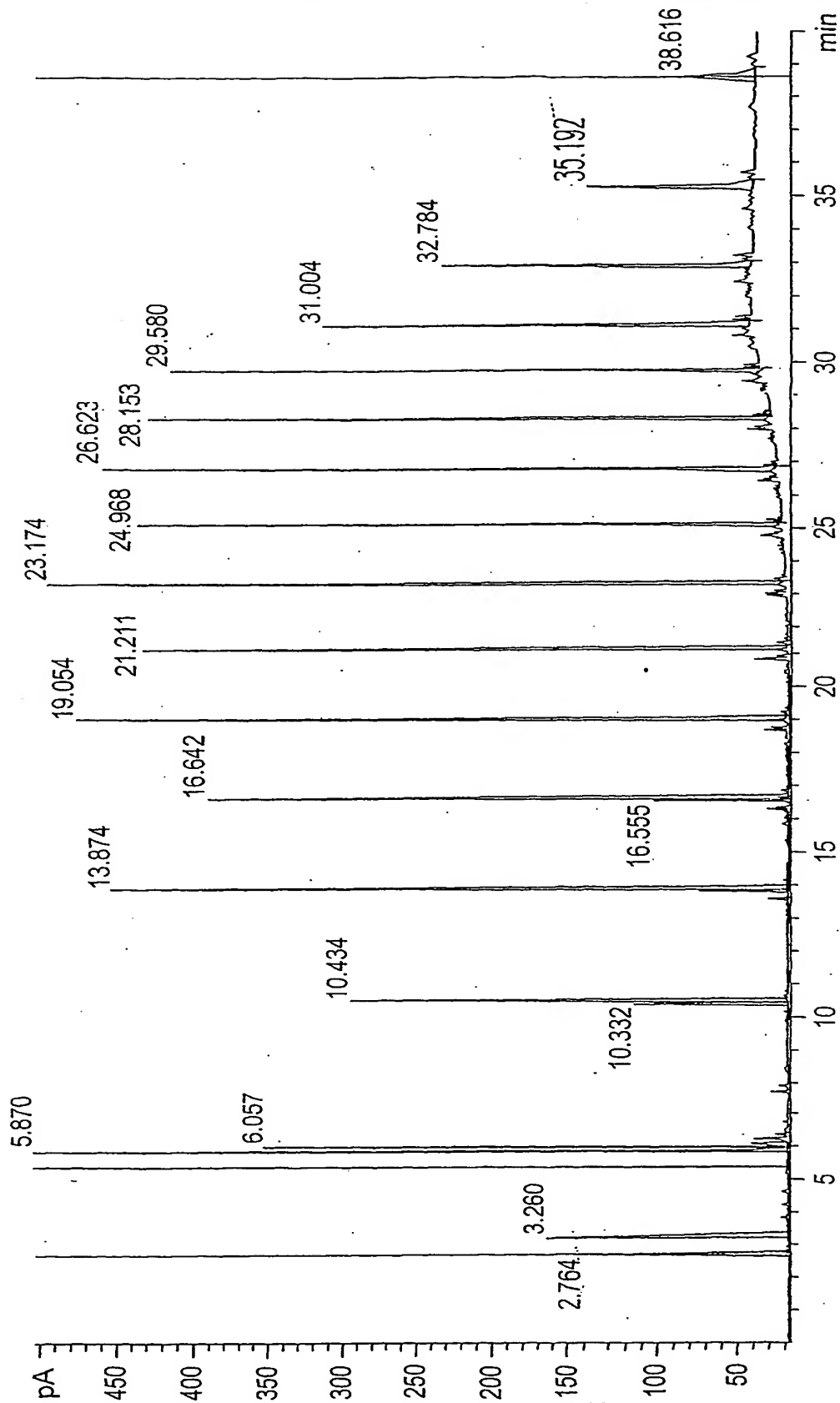
Fig.5 (Example 11)



6/15

10/549314

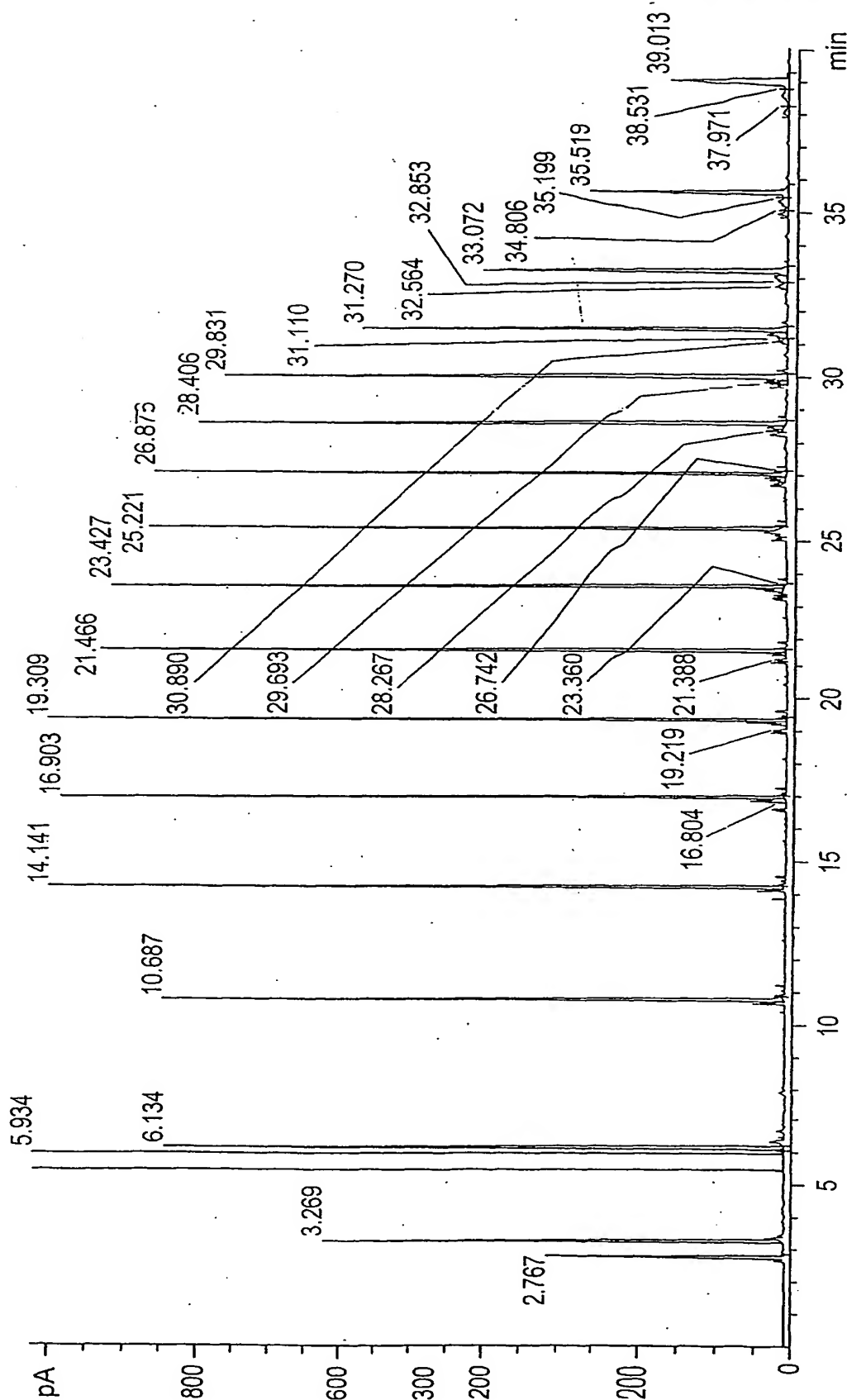
Fig.6 The GC trace for the soluble fraction from Example 14 is shown below.



7/15

10/549314

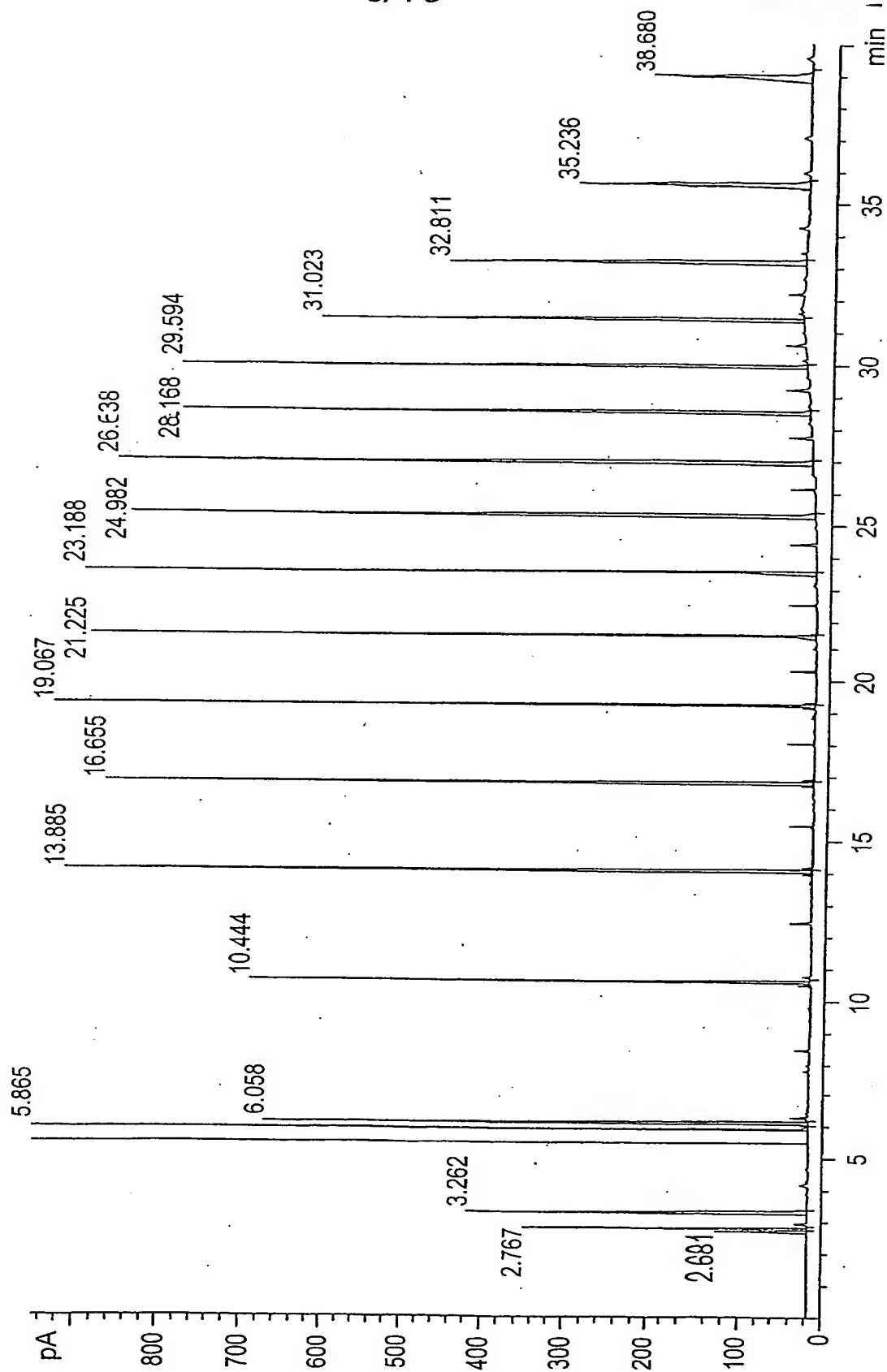
Fig. 7 The GC trace for the soluble fraction from Example 16 is shown below



8/15

10/549314

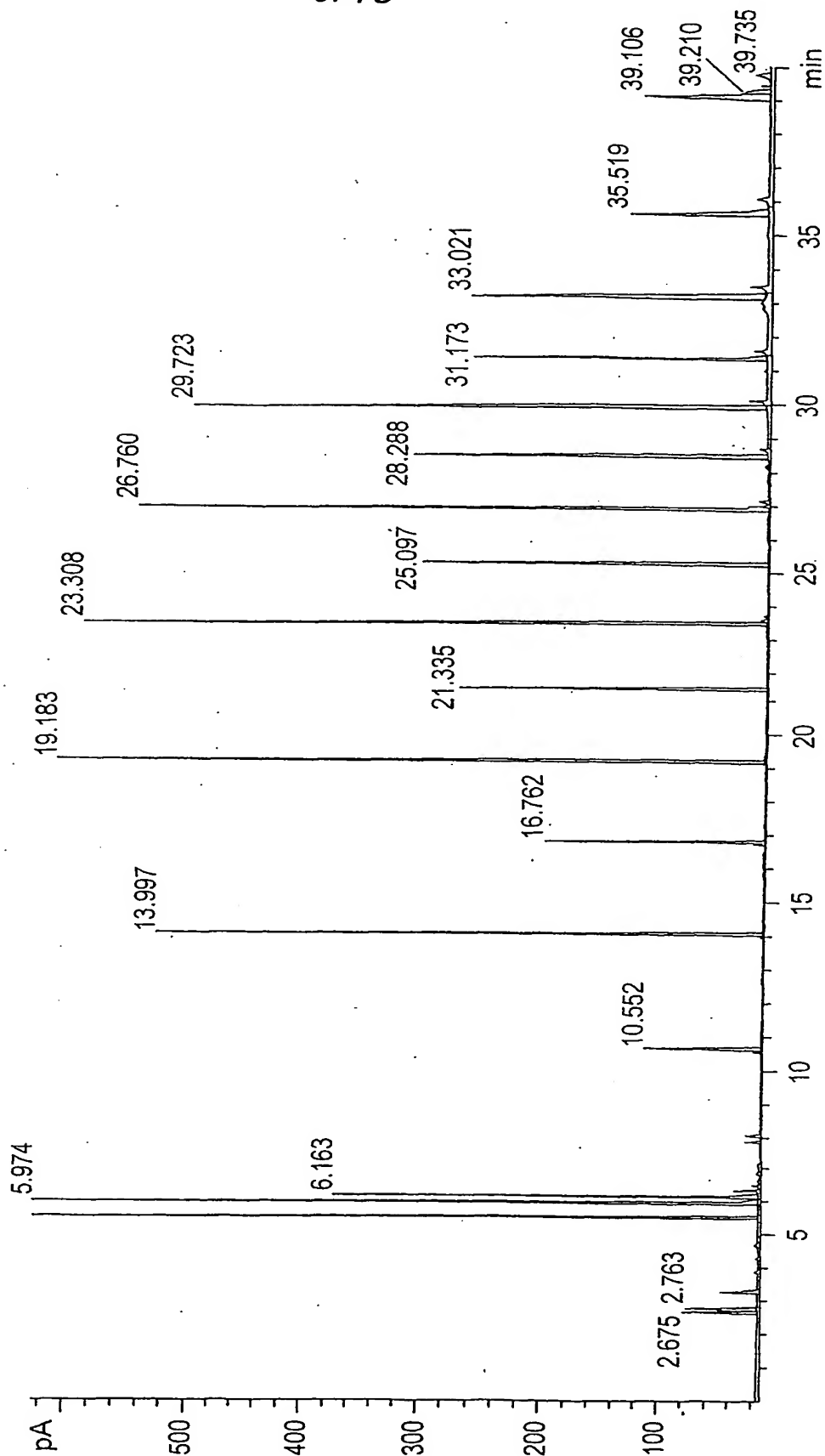
Fig.8 The GC trace for the soluble fraction from Example 19 is shown below



10/549314

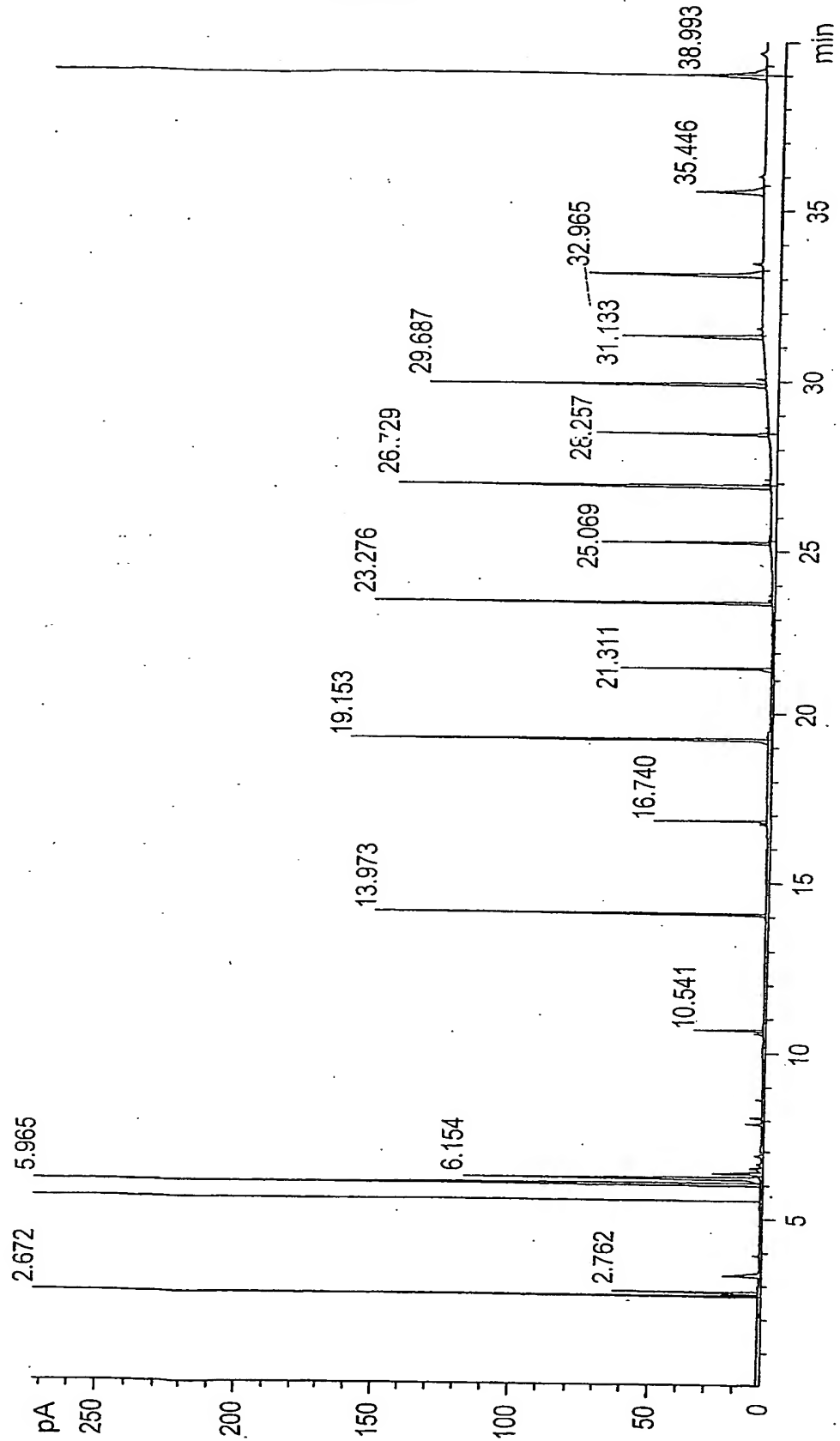
9/15

Fig.9 The GC trace for the soluble fraction from Example 20 is shown below



10/549314

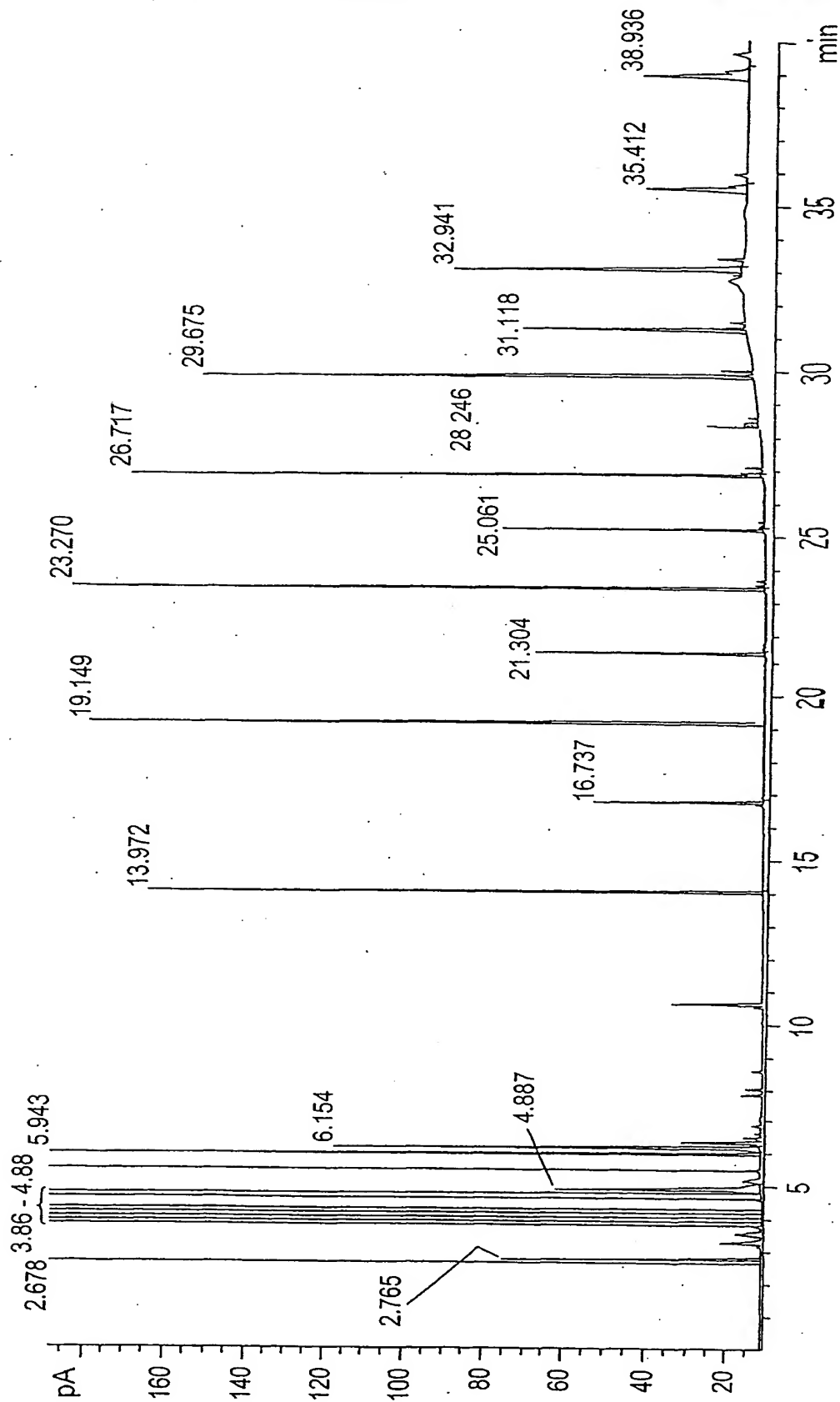
10/15

Fig.10 GC curves for the soluble fraction of Example 21

11/15

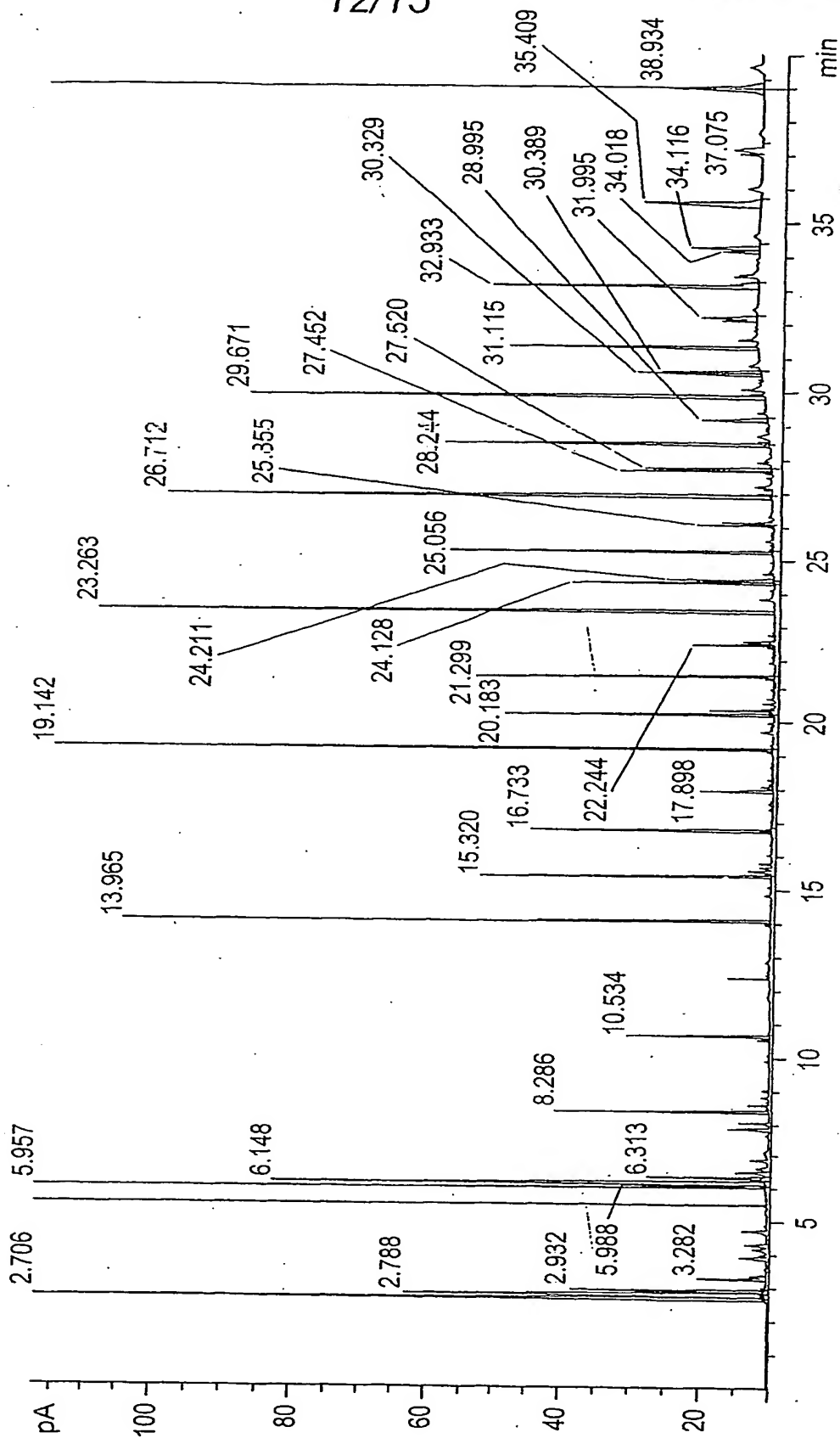
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Fig.11 Example 22 (presence of hexanes due to the co-catalyst solution; retention times 3.86 - 4.88 min).



10/549314

12/15

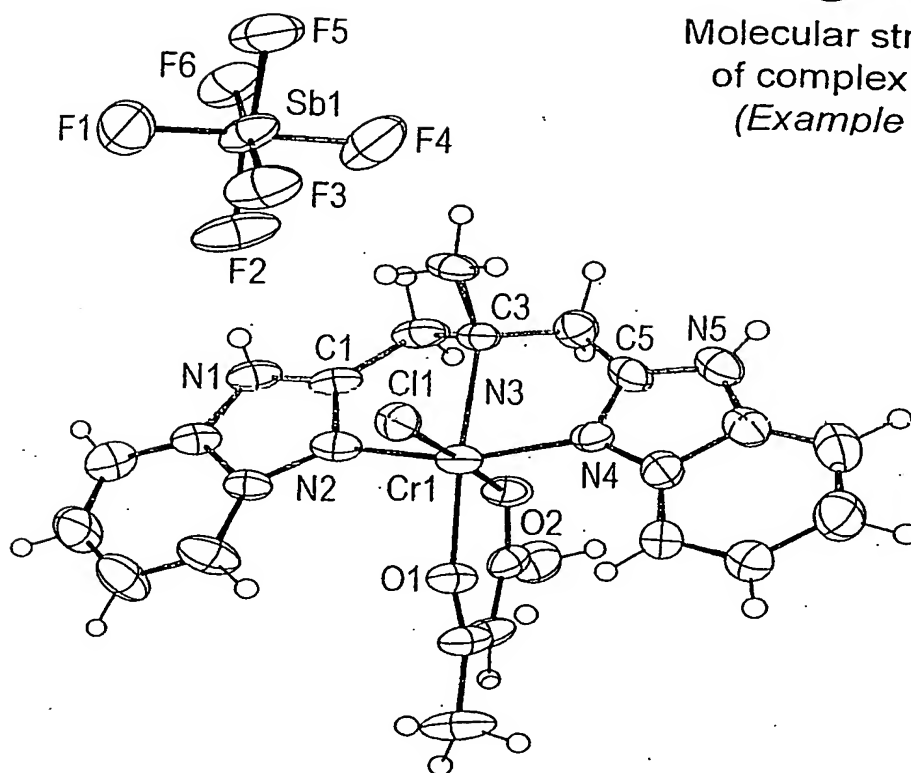
Fig.12 GC trace of solubles from Example 23

13/15

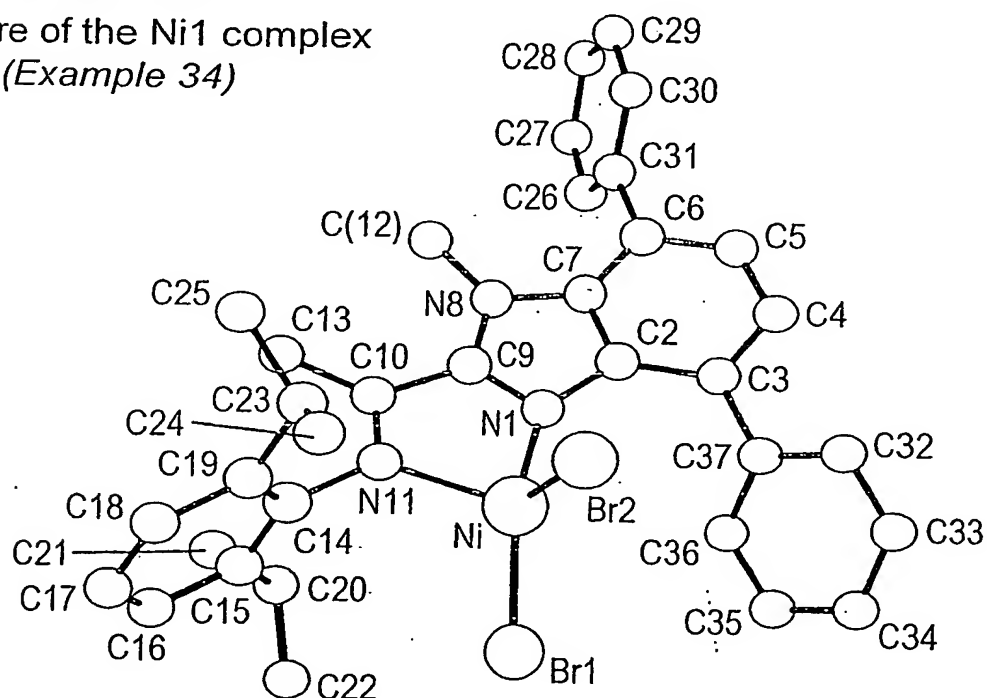
10/549314

Fig.13

Molecular structure
of complex Cr-7
(Example 26)

**Fig.14**

Structure of the Ni1 complex
(Example 34)

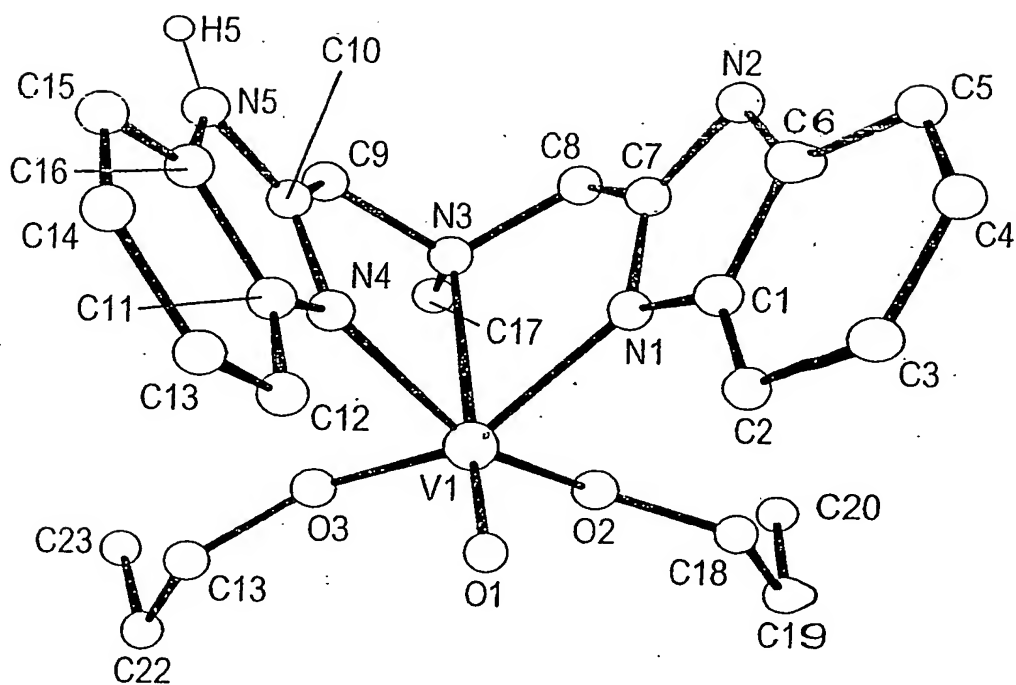


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14/15

Fig.15

Crystal structure of V-2
(Example 70)



10/549314

15/15

Fig.16

Ethylene uptake as a function of time for Example 77

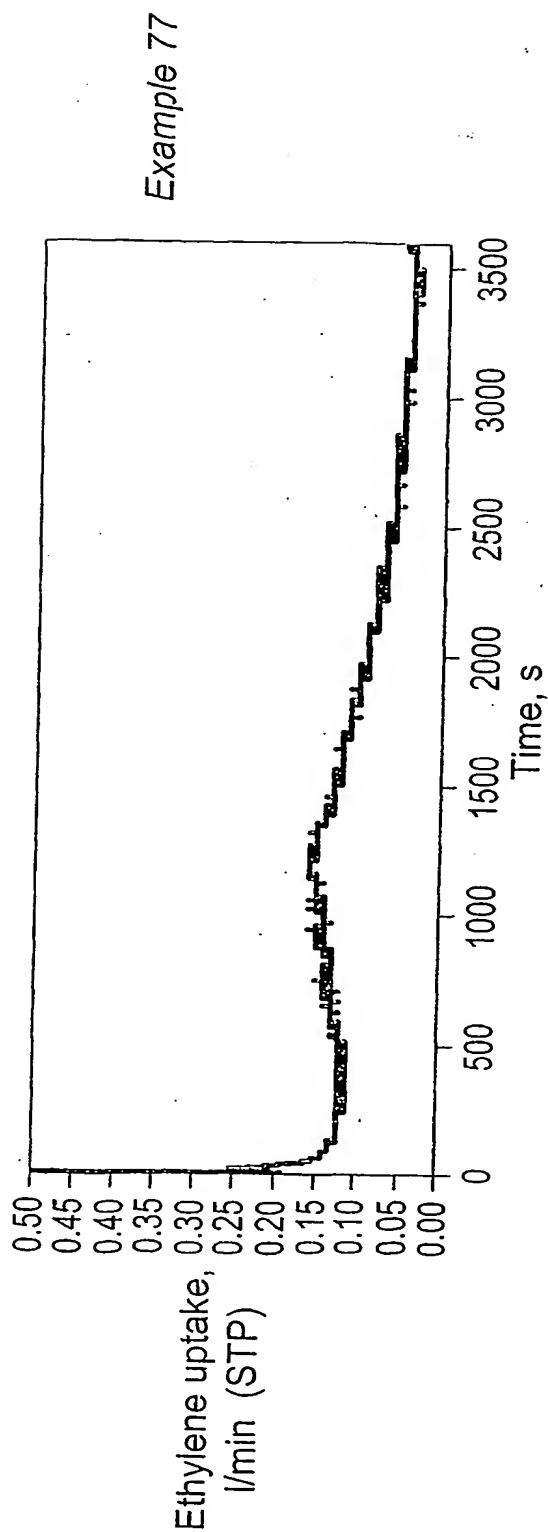
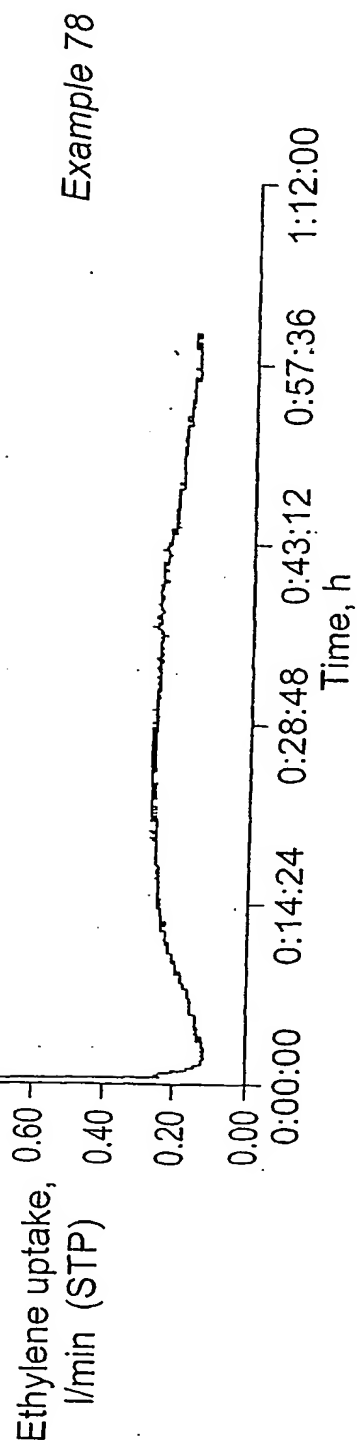


Fig.17

Ethylene uptake as a function of time for Example 78



INTERNATIONAL SEARCH REPORT

PCT/GB2004/001184

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F10/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 01/74831 A (ROMANO ANNA MARIA ; ENICHEM SPA (IT); PROTO ANTONIO (IT); SANTI ROBERT) 11 October 2001 (2001-10-11) the whole document	1-21, 23-34
X	WO 00/69923 A (DEVORE DAVID D ; DOW CHEMICAL CO (US); FRAZIER KEVIN A (US); PATTON JA) 23 November 2000 (2000-11-23) examples 12-19	1-21, 23-34
X	US 6 281 303 B1 (KILLIAN CHRISTOPHER MOORE ET AL) 28 August 2001 (2001-08-28) examples 1-6; compounds C1,C2,C5,C14,L1,L5,L7,L16	1-21, 23-34
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

8 June 2004

Date of mailing of the international search report

16/06/2004

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Balmer, J-P

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>PATENT ABSTRACTS OF JAPAN vol. 2000, no. 11, 3 January 2001 (2001-01-03) -& JP 2000 219704 A (TOSOH CORP), 8 August 2000 (2000-08-08) abstract</p>	<p>1-21, 23-34</p>

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